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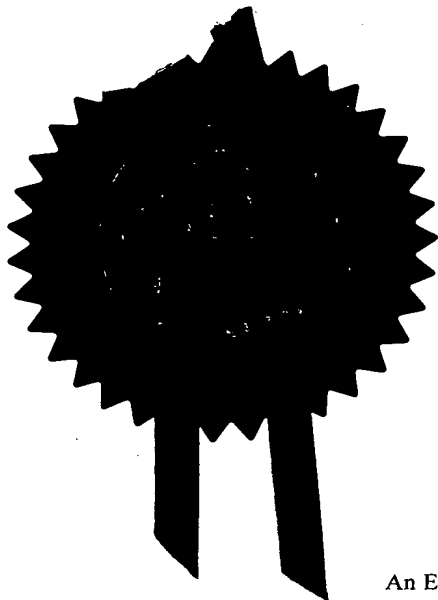
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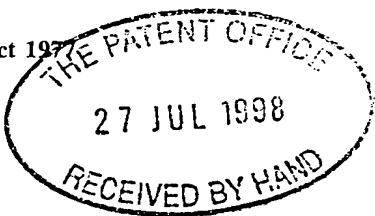
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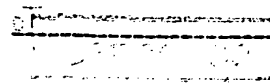
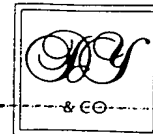
Patents Form 1/77

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P01/7700 25.00 - 9816348.8

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27 JUL 1998

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2.	Patent application number (The Patent Office will fill in this part)	9816348.8		
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3.	Full name, address and postcode of the or of each applicant (underline all surnames)	IMPERIAL COLLEGE OF SCIENCE, TECHNOLOGY & MEDICINE Sherfield Building Exhibition Road London SW7 2AZ United Kingdom		
	Patents ADP number (if you know it)	5808668001		
	If the applicant is a corporate body, give the country/state of its incorporation	United Kingdom		
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4.	Title of the invention	SMART COATING		
<hr/>				
5.	Name of your agent (if you have one)	D YOUNG & CO		
	"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	21 NEW FETTER LANE LONDON EC4A 1DA		
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Description 3

Claims(s) NONE

Abstract NONE

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Priority documents NONE

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Statement of inventorship and right to grant of a patent (Patents Form 7/77) NONE

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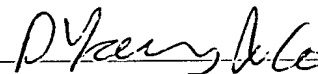
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>Concluding Remarks

>

>A new smart coating to provide surface temperature information, thermal insulation and coating erosion information is proposed. This coating incorporates the known properties of thermographic phosphors and TBC's and utilises demonstrated procedures for rare earth ion doping but is novel in the provision of a new multi-function coating. Such smart coating can be applied for a wide range of engineering applications

>A patented coating technique already exists within the college and may be utilised. However, this is not the novel aspect of the current proposal and other alternative coating techniques may be used.

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Smart Coating

>Summary

>

>A new 'smart' coating for use on high temperature components in gas turbine combustion chambers and on downstream turbine components is proposed. This coating will enable in service surface temperature monitoring and will also act as a protective thermal barrier coating with in service, on-line monitoring of coating integrity to give advanced warning of failure and enable timely remedial maintenance.

>

>Introduction/Applications

>

>The flame temperature in a gas turbine combustion chamber is often higher than the melting point of the materials from which the combustor is constructed. This presents a significant problem regarding the protection of components in and around the combustion chamber and is solved by the provision of a flow of cooling air over these surfaces and/or by using a protective thermal barrier coating (TBC). A considerable amount of development time is spent establishing the temperatures experienced by the various components in and around combustion chamber and the effectiveness of the cooling/protection schemes employed. The proposed new coating will act as a TBC and at the same time show temperature sensitive luminescent properties thereby acting as a surface temperature sensor. It will therefore enable the surface temperature distribution to be measured during development testing without the need for additional instrumentation and additionally can continue to be used in service to monitor surface temperatures to ensure the continuing performance of the cooling systems and indicate impending failure thereof.

>TBC coatings consist of a **thick** layer of refractory material (typically yttria stabilised zirconia) with a low thermal conductivity (around 1-3 W/mK) which provide significant resistance to heat transfer thereby reducing the temperature experienced by the coated components. One of the main problems associated with TBC's is obtaining good adhesion between the coating and metal surface and this plays an important part in the lifetime of the coating along with other factors such as erosion. To-date there no reliable

model exists for determining the lifetime of TBC's so that inspection is necessary with attendant maintenance costs. The proposed smart coating will enable in service monitoring of coating erosion and thermal shock resistance to provide an early indication of failure and enable timely remedial maintenance to be carried out.

>

>Theory

>

>The temperature sensitive luminescent characteristics of thermographic phosphors (TP's) when illuminated with UV light has been known for a number of years. These phosphors typically consist of a ceramic host (eg Y₂O₃ or YAG) doped with a rare earth ion (eg Eu, Tb, Dy). When illuminated with UV light their phosphorescent emission shows sensitivity to the local temperature in one or combination of the following two ways. Firstly the emission spectrum of the phosphors may change, and here, the ratio of the intensities of certain emission lines may be used as a temperature measure. Secondly, when illumination ceases the emission from the phosphors decays exponentially with a time constant which is temperature sensitive and which can, therefore, also be used as a temperature measure.

>The inventive step in the proposed smart coating is the incorporation of a thermographic phosphor into a TBC to create an thermal insulating layer with temperature sensing properties. The incorporation of the TP's within a TBC can be achieved in one or combination of the following five methods:

(i) Firstly a multilayer coating consisting of a traditional TBC overlaid with a TP layer could be used. Multi-layer TBC's already exist but the layering is undertaken to improve mechanical and thermal properties of the coating and not to include a sensing element.

(ii) The second method is to dope the zirconia with a temperature sensing rare earth ion such as Eu partially or wholly replacing the original stabilising dopant such as yttria and creating a multi-function coating system. The doping of yttria stabilised zirconia with europium has already been demonstrated. However, it has not been used as a temperature sensor nor as a surface coating or a TBC.

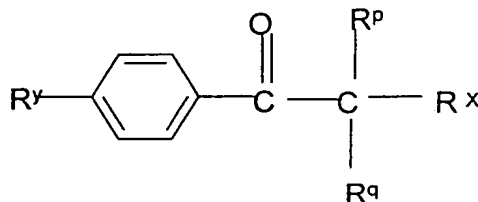
(iii) The third method is to deposit functionally graded coatings consisting of TBC and TP with systematic variation in the composition of the temperature sensing rare earth ion such as Eu across the coating thickness (i.e. from the substrate to the outermost coating)

(iv) The fourth method is to deposit multilayer coatings consisting of alternating layer of TBC with TP, and TP layer.

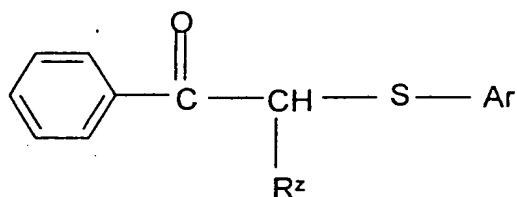
(v) The fifth method is a composite coating consisting of TP reinforced TBC coating.

Using the above techniques it should be possible to create a coating which provides thermal insulation whilst at the same time enabling the surface temperature to be measured. The measurement of coating erosion can be achieved using a multiple layer approach. By using different dopants or dopant concentrations in successive layers the emission properties of the layers can be changed. Hence erosion of successive layers will be accompanied by a detectable change in the emission characteristics.

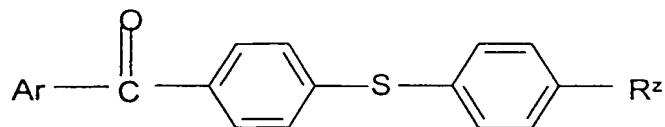
dimethylhydroxyacetophenone (sold under the Trade name "Darocure 1173"); substituted dialkylhydroxyacetophenone alkyl ethers such compounds of formula



where R^y is alkyl and in particular 2,2-dimethylethyl, R^x is hydroxy or halogen such as chloro, and R^p and R^q are independently selected from alkyl or halogen such as chloro (examples of which are sold under the Trade names "Darocure 1116" and "Trigonal P1"); 1-benzoylcyclohexanol-2 (sold under the Trade name "Irgacure 184"); benzoin or derivatives such as benzoin acetate, benzoin alkyl ethers in particular benzoin butyl ether, dialkoxybenzoins such as dimethoxybenzoin or deoxybenzoin; dibenzyl ketone; acyloxime esters such as methyl or ethyl esters of acyloxime (sold under the trade name "Quantaqure PDO"); acylphosphine oxides, acylphosphonates such as dialkylacylphosphonate, ketosulphides for example of formula



where R^z is alkyl and Ar is an aryl group; dibenzoyl disulphides such as 4,4'-dialkylbenzoyldisulphide; diphenyldithiocarbonate; benzophenone; 4,4'-bis(N,N-dialkylamino)benzophenone; fluorenone; thioxanthone; benzil; or a compound of formula



where Ar is an aryl group such as phenyl and R^z is alkyl such as methyl (sold under the trade name "Speedcure BMDS").

The compound may be polymerised under the influence of a free radical or ion initiator as is understood in the art, as well as by application of an electron beam.

As used herein, the term "alkyl" refers to straight or branched chain alkyl groups, suitably containing up to 20 and preferably up to 6 carbon atoms. The term "alkenyl" and "alkynyl" refer to unsaturated straight or branched chains which include for example from 2-20 carbon atoms, for example from 2 to 6 carbon atoms. In addition, the term "aryl" refers to aromatic groups such as phenyl or naphthyl.

The term "hydrocarbyl" refers to any structure comprising carbon and hydrogen atoms. For example, these may be alkyl, alkenyl, alkynyl, aryl such as phenyl or naphthyl, aralkyl, cycloalkyl, cycloalkenyl or cycloalkynyl. Suitably they will contain up to 20 and preferably up to 10 carbon atoms. The term "heterocyclyl" includes aromatic or non-aromatic rings, for example containing from 4 to 20, suitably from 5 to 10 ring atoms, at least one of which is a heteroatom such as oxygen, sulphur or nitrogen. Examples of such groups include furyl, thienyl, pyrrolyl, pyrrolidinyl, imidazolyl, triazolyl, thiazolyl, tetrazolyl, oxazolyl, isoxazolyl, pyrazolyl, pyridyl, pyrimidinyl, pyrazinyl, pyridazinyl, triazinyl, quinolinyl, isoquinolinyl, quinoxalinyl, benzthiazolyl, benzoxazolyl, benzothienyl or benzofuryl.

The term "functional group" refers to reactive groups such as halo, cyano, nitro, oxo, $\text{C}(\text{O})_n\text{R}^a$, OR^a , $\text{S}(\text{O})_n\text{R}^a$, NR^bR^c , $\text{OC}(\text{O})\text{NR}^b\text{R}^c$,

$C(O)NR^bR^c$, $OC(O)NR^bR^c$, $-NR^7C(O)_nR^6$, $-NR^aCONR^bR^c$, $-C=NOR^a$, $-N=CR^bR^c$, $S(O)_tNR^bR^c$ or $-NR^bS(O)_tR^a$ where R^a , R^b and R^c are independently selected from hydrogen or optionally substituted hydrocarbyl, or R^b and R^c together form an optionally substituted ring which optionally contains further heteroatoms such as $S(O)_s$, oxygen and nitrogen, t is an integer of 1 or 2, t is 0 or an integer of 1-3.

The term "heteroatom" as used herein refers to non-carbon atoms such as oxygen, nitrogen or sulphur atoms. Where the nitrogen atoms are present, they will generally be present as part of an amino residue so that they will be substituted for example by hydrogen or alkyl.

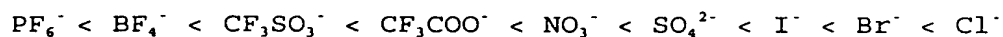
The term "amide" is generally understood to refer to a group of formula $C(O)NR^aR^b$ where R^a and R^b are hydrogen or an optionally substituted hydrocarbyl group.

The nature of the electron withdrawing group or groups used in any particular compound of formula (I) will depend upon its position in relation to the double bond it is required to activate, as well as the nature of any other functional groups within the compound.

In a preferred embodiment, R^1 and R^6 form an electron withdrawing group. For example, R^1 is a heteroatom or a substituted heteroatom which has electron withdrawing properties, for example a group $N^+R^{12}(Z^{m-})_{1/m}$, $S(O)_pR^{13}$, B , $P(O)_qR^{14}$ or $Si(R^{15})$ where R^{12} , R^{13} , R^{14} and R^{15} are independently selected from hydrogen or hydrocarbyl, Z is an anion of valency m , p is 0, 1 or 2, and q is 0, 1, 2 or 3; and R^6 is a bond: or R^1 is a group CH and R^6 is a group $-C(O)O-$ or $-OC(O)-$. Most preferably, R^1 is a group $N^+R^{12}(Z^{m-})_{1/m}$, $S(O)_pR^{13}$, B , $P(O)_qR^{14}$ or $Si(R^{15})$ where R^{12} , R^{13} , R^{14} and R^{15} are independently selected

from hydrogen or alkyl in particular C_{1-3} alkyl, Z is a halogen
In particular R^1 is a group $N^+R^{12}(Z^{m-})_{1/m}$, and R^6 is a bond

The nature of the anion Z will affect the physical properties of the final polymer such as its porosity, water retention and in particular, its conductivity. Suitable anions for the Z group include halide ions such as fluoride, chloride, bromide or iodide, borides such as boron tetrafluoride; carboxylic acid esters such as those of formula $R^{14}C(O)O^-$ where R^{14} is an optionally substituted hydrocarbyl group such as haloalkyl, in particular trifluoromethyl; and other anionic groups such as mesylate and tosylate. In general, the water permeability of the ultimate polymer will vary as follows:



Other factors which affect the water permeability of the polymer is the nature of the bridging group. When this contains for example perhaloalkyl substituents such as perfluoroalkyl, it will be largely water impermeable as compared to polymers which have alkylene bridging groups optionally interposed with say oxygen.

Most preferably, the combination of R^1 and R^6 forms an amide group, where R^1 is a nitrogen atom and R^6 is a carbonyl group.

Alternatively, where the activation is effected by electron withdrawing groups at a position indicated by R^2 or R^3 , suitable electron withdrawing groups R^9 and R^{10} include $COCH_2CN$ and $COCH_3$, preferably R^9 and R^{10} together form an oxo group.

Where R^{11} is an electron withdrawing group, it is suitably $COCH_3$.

Preferably, X^1 , X^2 , Y^1 and Y^2 are all hydrogen.

Suitably r is an integer of from 2 to 6, preferably from 2 to 4. The polymers produced can be useful in a number of different applications including the production of network polymers and those used in thermal management.

Thermal management is the control of optical properties of materials across solar and thermal wavebands (~ 0.7 -12 microns). This control of transmitted, reflected and absorbed radiation gives the potential to design systems that can selectively perform different tasks at different wavelengths. For example use of silver coatings by the glazing industry to limit solar transmission (material transparent at visible wavelengths but reflective across the solar) and thus prevent 'greenhouse' heating. Other example could be solar water heaters where the material is transparent at NIR wavelengths but reflective at longer wavelengths. Benefits of thermal management could be in reduced air conditioning/heating costs.

The properties of the polymer obtained in accordance with the invention will depend upon a variety of factors but will depend very largely on the nature of the group R^{16} .

Suitably R^{16} will comprise a bridging group for example as is known in polymer, paint or coating chemistry. These may include straight or branched chain alkyl groups, optionally substituted or interposed with functional groups or siloxane groups such as alkyl siloxanes. Suitable bridging groups include those found in polyethylenes, polypropylenes, nylons, as listed in Table 1.

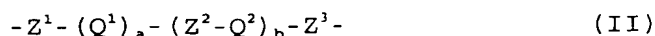
Table 1

Polymer type	Repeat Unit of Bridging Group
Polyethylene	CH_2
Polystyrene	$\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)$ where the phenyl ring is optionally substituted
Polyisobutylene	$\text{CH}_2\text{CH}(\text{CH}(\text{CH}_3)_2)$
Polyisoprene	$\text{CH}_2\text{CH}(\text{CH}_3)$
Polytetrafluoroethylene	$\text{CH}_2(\text{CF}_2)_x\text{CH}_2$
Polyvinylidene fluoride	$\text{CH}_2(\text{CF}_2\text{CH}_2)_x$
polyethyleneoxide	$(\text{OCH}_2\text{CH}(\text{CH}_3))_x\text{O}$
Nylon	$\text{CH}_2(\text{NHCOCH}_2)_x\text{CH}_2$
Peptide	$\text{CH}_2(\text{NHCOCH}_R)_x\text{CH}_2$
Polyurethanes	
Polyesters	
Polysiloxanes	
Polyacrylates	

The length of the bridging group will affect the properties of the polymeric material derived from this. This can be used to design polymers with properties which are best suited to the application. For instance when the bridging group comprises relatively long chains, the polymer will have pliable plastic properties. Alternatively, when the bridging group is relatively short, the material will be more brittle.

Other possibility for producing particular properties arises from the possibility of producing copolymers where another monomeric compound, for example one which is not of formula (I), is mixed with the compound of formula (I) prior to polymerisation. Such monomers are known in the art.

Examples of possible bridging groups R^{16} where r is 2 are groups of sub-formula (II)



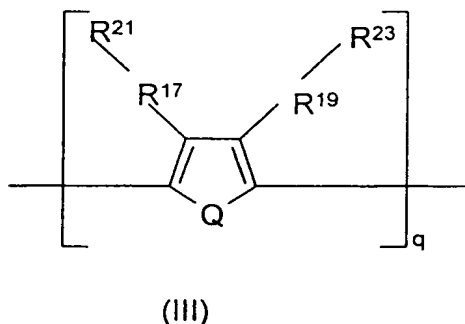
where a and b are independently selected from 0, 1 or 2, Z^1 , Z^2 and Z^3 are independently selected from a bond, an optionally substituted linear or branched alkyl or alkene chain wherein optionally one or more non-adjacent carbon atoms is replaced with a heteroatom or an amide group, Q^1 and Q^2 are independently selected from an optionally substituted carbocyclic or heterocyclic ring which optionally contains bridging alkyl groups; a and b are independently selected from 0, 1 or 2.

Suitable carbocyclic rings for Q^1 and Q^2 include cycloalkyl groups for example of from 1 to 20 carbon atoms. Bridged carbocyclic ring structures include 1,4-bicyclo[2.2.2]octane, decalin, bicyclo[2.2.1]heptane, cubane, diadamantane, adamantane. Suitable heterocyclic rings include any of the above where one or more non adjacent carbon atoms are replaced by a heteroatom such as oxygen, sulphur or nitrogen (including amino or substituted amino), or a carboxyl or an amide group. Suitable optional substituents for the groups Q^1 and Q^2 include one or more groups selected from alkyl, alkenyl, alkynyl, aryl, aralkyl such as benzyl, or functional groups as defined above. Particularly substituents for the groups Q^1 and Q^2 are oxo and halogen in particular fluorine and chlorine.

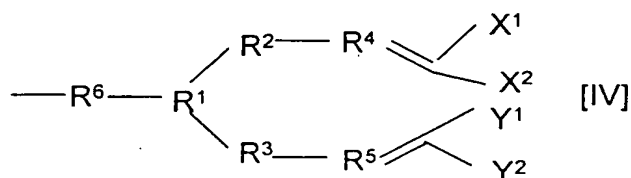
Suitable optional substituents for the alkyl and alkene groups Z^1 , Z^2 and Z^3 include aryl, aralkyl and functional groups as defined above. Particular substituents include halogens such as fluorine and chlorine, and oxo.

Other sorts of bridging groups R^{16} include electrically conducting chains, for instance, electrically conducting unsaturated chains such as alkenes or chains incorporating

aromatic or heterocyclic rings. For instance, the group R^{16} in a compound of formula (I) may comprise a di substituted conducting unit such as a tertathiafulvalene. Thus an example of a compound of formula (I) is a compound of formula (III)



where R^{21} and R^{23} are each groups of sub-formula (IV)



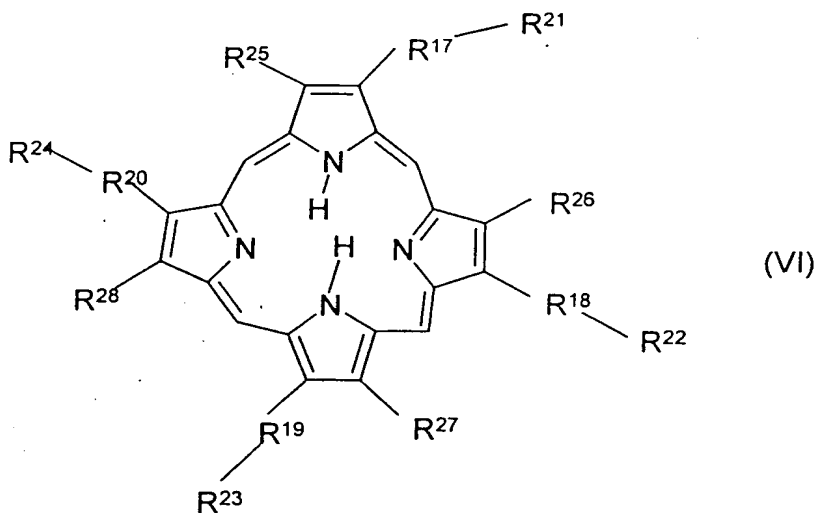
where X^1 , X^2 , Y^1 , Y^2 , R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are as defined in relation to formula (I) above and R^{17} and R^{19} are independently selected from groups of sub-formula (II) as given above, q is an integer of 1 or more, for example from 1 to 6, and Q is sulphur or NH. In particular R^{17} , R^{18} , R^{19} and R^{20} are alkyl groups.

Polymerisation of compounds of formula (III) will give cross-linked networks where the cross-linking occurs through the diene units. This will lead to a very stable material with robust physical properties. Once again, varying the length of the spacer groups R^{17} , R^{18} , R^{19} and R^{20} , will lead to materials with designer properties. For instance when R^{17} , R^{18} , R^{19} and R^{20} are relatively long chains, the polymer will have pliable

plastic properties. Alternatively, when the chains R^{17} , R^{18} , R^{19} and R^{20} are relatively short, the material will be more brittle.

Where R^1 and R^6 together form a group $-N^+R^7Z^-$, varying the counter ion Z^- can also be used to adjust the physical properties of the polymer, such as water retention, porosity or conductivity. The materials will exhibit conducting properties, making them suitable as organic semiconductors for example for use as interconnects for IC chips etc.

Alternatively, a bridging group R^{16} may comprise a tetra or octa substituted non-linear optic unit such as an optionally substituted porphyrin or phthalocyanine wherein the optional substituents are hydrocarbyl groups such as alkyl in particular methyl. An example of such a compound is a compound of formula (VI)



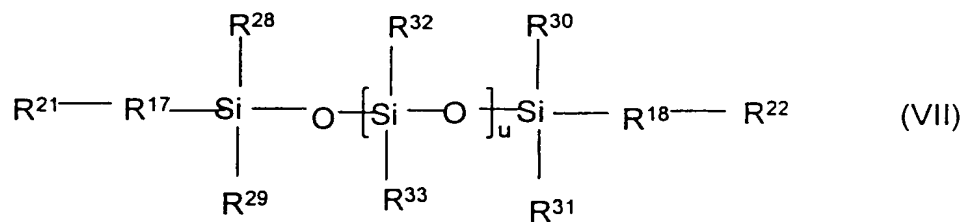
where R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , R^{23} and R^{24} are as defined in relation to formula (III) above and R^{25} , R^{26} , R^{27} and R^{28} are each independently selected from hydrogen or hydrocarbyl groups such as alkyl and in particular methyl; and the compound

optionally contains a metal ion within the macrocyclic heterocyclic unit.

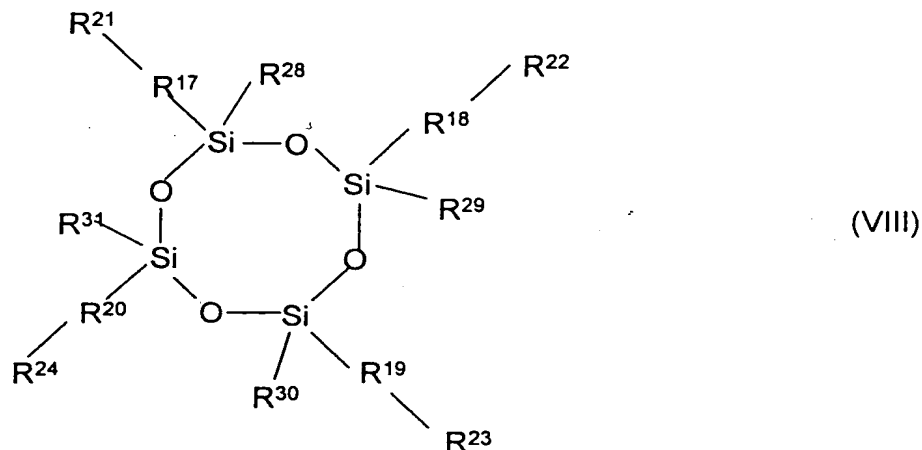
Polymerisation of a compound of formula (VI) in accordance with the scheme of Figure 1, for example by photopolymerisation will provide a cross linked network polymer where the cross linking occurs through the diene units for example as either quaternary ammonium salts or amides depending upon the particular nature of the groups R^1 and R^6 present in the R^{21} , R^{22} , R^{23} and R^{24} units. Again this can produce a very stable network or elastomeric material with robust physical properties. In addition to conductivity, these polymers will be capable of exhibiting third order polarisabilities and they will be suitable for applications which employ the Kerr effect. These properties can be affected or moderated when metals or metal ions are inserted into the macrocyclic heterocyclic unit. Suitable metal ions include sodium, potassium, lithium, copper, zinc and iron ions.

Yet a further possibility for the bridging group R^{16} is a polysiloxane network polymer where R^{16} comprises a straight or branched siloxane chain of valency r or a cyclic polysiloxane unit.

Thus compounds of structure (VII)



where R^{17} , R^{18} , R^{21} and R^{22} are as defined above in relation to formula (III), R^{28} , R^{29} , R^{30} are R^{31} , are selected from hydrocarbyl such as alkyl and in particular methyl, and each R^{32} or R^{32} group is independently selected from hydrocarbyl or a group of formula R^{19} - R^{23} where R^{19} and R^{23} are as defined above in relation to formula (III), and u is 0 or an integer of 1 or more, for example of from 1 to 20; and (VIII)



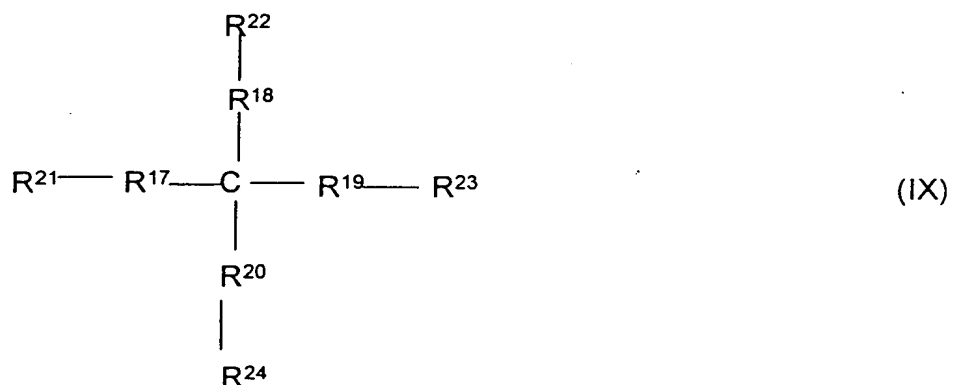
where R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , R^{23} and R^{24} are as defined above in relation to formula (III) and R^{28} , R^{29} , R^{30} and R^{31} are as defined above in relation to formula (VII). Although formula (VIII) has been illustrated with four siloxane units in the ring, it will be appreciated that there may be other numbers of such units in the cyclic ring, for example from 3 to 8, preferably from 3 to 6 siloxane units.

In the above structures (XI) and (XII), it will be appreciated that $-\text{Si}-$ may be replaced by B or B^+ ; or $-\text{Si}-\text{O}-$ is replaced by $-\text{B}-\text{N}(\text{R}^{40})-$ where R^{40} is a hydrocarbyl group such as those defined above in relation to group R^{32} in formula (XI) or a group $-\text{R}^{24}-\text{R}^{28}$ as defined in relation to formula (XII) above.

Upon polymerisation, compounds of formula (VII) and (VIII) or variants thereof, will form a cross-linked network where the cross-linking occurs through the groups R^{21} , R^{22} , R^{23} and R^{24} as

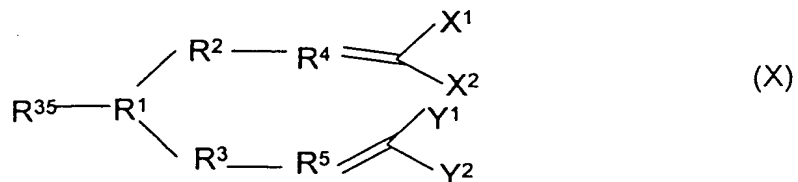
illustrated in Figure 1. Such polymers may exhibit properties similar to those of conventional siloxanes. However, in the case of compounds of formula (VII) and (VIII), they may be coated onto surfaces and polymerised in situ, for example using radiation curing.

Further examples of compounds of formula (I) include compounds of formula (IX)



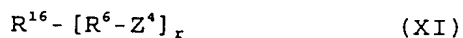
where R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , R^{23} and R^{24} are as defined above in relation to formula (III).

Compounds of formula (I) are suitably prepared by conventional methods, for example by reacting a compound of formula (X)



where X^1 , X^2 , Y^1 , Y^2 , R^2 , R^3 , R^4 and R^5 are as defined in relation to formula (I), R^1 is a group R^1 as defined in relation to

formula (I) or a precursor thereof, R^{35} is hydrogen or hydroxy, with a compound of formula (XI)



where R^6 , R^{16} and r are as defined in relation to formula (I) and Z^4 is a leaving group, and thereafter if desired or necessary converting a precursor group $R^{1'}$ to a group R^1 .

Suitable leaving groups Z^4 include halogen, in particular bromo, mesylate or tosylate. The reaction is suitably effected in an organic solvent such as tetrahydrofuran, dichloromethane, toluene, an alcohol such as methanol or ethanol, or a ketone such as butanone and at elevated temperatures for example near the boiling point of the solvent.

Preferably the reaction is effected in the presence of a base such as potassium carbonate.

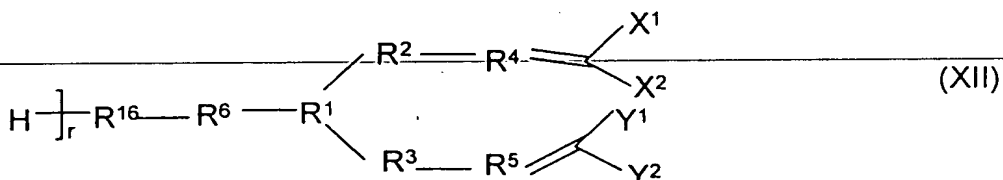
When the group $R^{1'}$ is a precursor of the group R^1 , it may be converted to the corresponding R^1 group using conventional techniques. For example $R^{1'}$ may be a nitrogen atom, which may be converted to a group $NR^{12}(Z^m)_{1/m}$ where R^{12} , Z and m are as defined above, by reaction with an appropriate salt under conventional conditions. Examples of this are illustrated hereinafter.

Compounds of formulae (X) and (XI) are either known compounds or they can be prepared from known compounds by conventional methods.

Thus the invention further provides a method for producing a polymeric material, said method comprising causing a compound

of formula (I) to polymerise. Suitably the compound of formula (I) is a radiation curable compound and polymerisation is effected by subjecting the compound to the appropriate radiation (e.g. heat or ultraviolet radiation) and if necessary in the presence of a suitable initiator such as a photoinitiator like AIBN. Where the compound of formula (I) cannot or it is not appropriate for it to be cured in this way, other conventional polymerisation techniques can be employed as would be understood in the art.

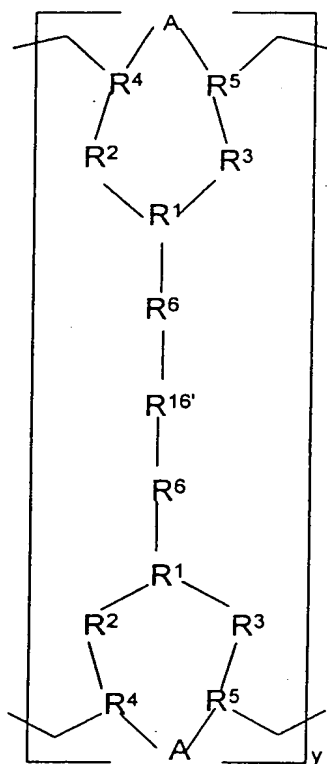
During the polymerisation process, the compounds of formula (I) link together by way of the diene group as illustrated in Figure 1. Because the compounds of formula (I) include at least two diene groups, they will tend to become cross linked to form a network or three dimensional structure. The degree of cross linking can be controlled by carrying out the polymerisation in the presence of cross-linkers, where for example r is greater than 2, for example 4, or diluents, plasticisers or chain terminators. The latter will suitably comprise a compound of formula (XII)



where X^1 , X^2 , Y^1 , Y^2 , R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^{16} and r are as defined in relation to formula (I). Compounds of formula (I) may be used in the preparation of homopolymers or copolymers where they are mixed with other monomeric units, which may themselves be of formula (I) or otherwise.

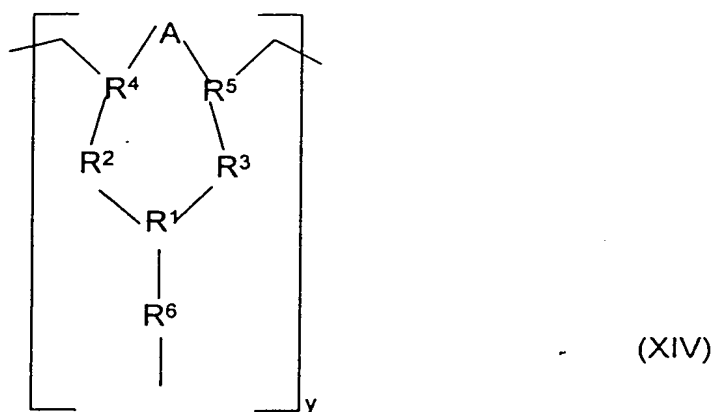
A general scheme illustrating the sort of polymerisation process which may occur using a polyethylene type bridging group is illustrated in Figure 2.

Polymeric compounds obtained form a further aspect of the invention. Thus the invention further provides a polymeric compound of formula (XIII)



(XIII)

where A is a bond or or CH_2 , R^1 , R^2 , R^3 , R^4 , R^5 , R^6 are as defined in relation to formula (I), $\text{R}^{16'}$ is a group of formula R^{16} as defined in formula (I) which may be substituted by further groups of sub formula (XIV)



and y is an integer in excess of 1, preferably in excess of 5 and suitably from 5 to 30 and A is as defined above. It will be understood that copolymers also fall within the scope of this definition as outlined above.

Using the compounds of the invention, it is possible to take a suitable organic system that has optimal or optimised properties for use in certain applications, eg, high yield strength, large hyperpolarisability, high pyroelectric coefficient, high conductivity etc, and to structurally modify the system so that it is possible to polymerise it. If functional groups are incorporated that will polymerise, it will become possible to create a three dimensional network or plastic that will have properties associated with the parent organic system.

The advantages of the compounds of the invention is that they allow for the possibility that they can be applied in the form of a paint and caused to polymerise in situ. Thus this allows for ease of processing. Further, by providing for the construction of networks as a result of the cross linking, the resultant polymer can be mechanically strong and durable.

The versatility of the systems of the invention mean that it is possible to build in anisotropy which would improve directional physical properties, eg NLO, mechanical yield

strength etc. Both amorphous or ordered systems can be prepared depending upon the particular polymerisation conditions used.

Copolymerisation is also possible which can be used advantageously to affect physical properties of the polymer obtained.

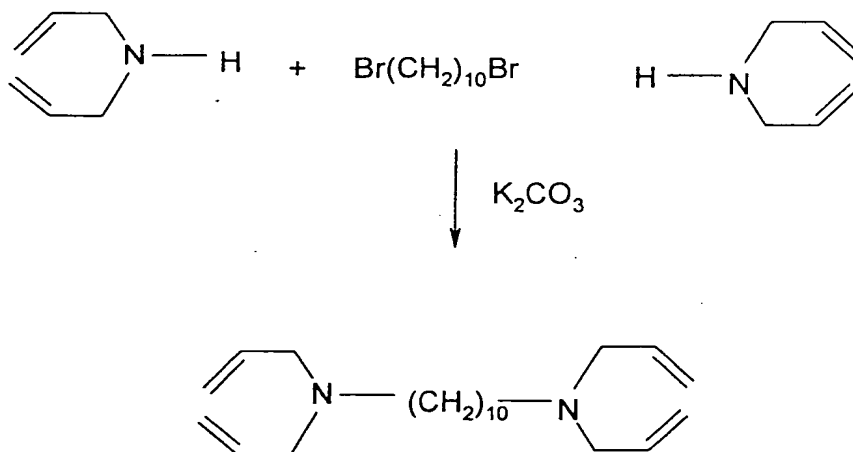
Systems can be prepared which mimic conventional polymers/elastomers, or which involve donor/acceptor systems.

Polymers of the invention are particularly suitable for the production of adhesive coatings, and multilayer coatings as well as binders. It is possible to manipulate the low molar mass coating before polymerisation is carried out, eg, poling etc.

The invention will now be particularly described by way of example with reference to the accompanying diagrammatic drawings in which:

Figure 1 illustrates the way in which compounds of the invention may cyclopolymerise; and

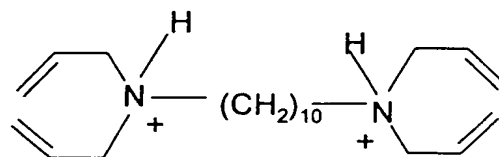
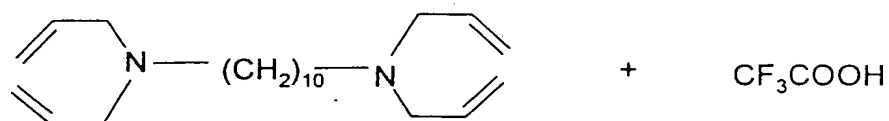
Figure 2 illustrates the production of a network polymer in accordance with the invention:

Example 1

Diallylamine (6.45g, 0.66mol), 1,10-dibromodecane (10.0g, 0.033mol) and potassium carbonate 9.70g, 0.66mol) were placed in ethanol (60cm³) and the mixture was refluxed for 10 hours. The solids were removed by filtration and the solvent removed in vacuo to leave a yellow oil. The oil was purified by column chromatography using silica gel and ethyl acetate to leave, after removal of solvent in vacuo, 9.80g, 89% of yellow oil.

¹HNMR (CDCl₃)δ: 1.15-1.30 (m, 12H), 1.35-1.45(m, 4H), 2.40(t, 4H), 3.10(d, 8H), 5.05-5.20(m, 8H), 5.30-5.55(m, 4H).

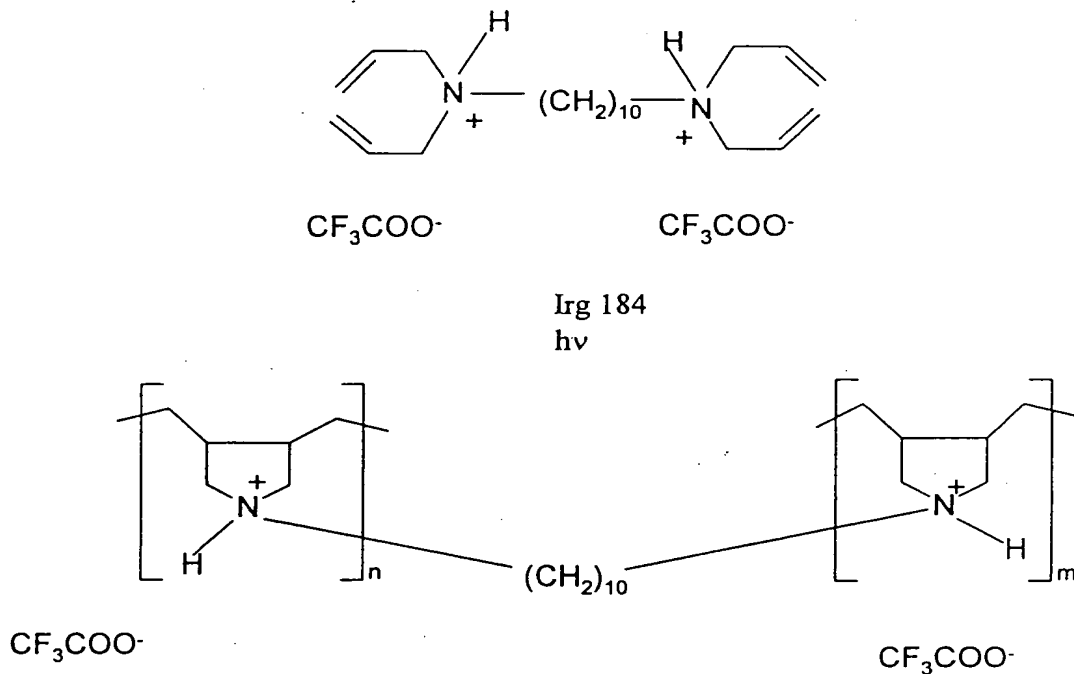
Ir v max (thin film): 2920, 2850, 2800, 1640, 1460, 1440, 1350, 1250, 1150, 1110, 990, 915cm⁻¹

Step 2 CF_3COO^- CF_3COO^-

The monomer from step 1 above (4.0g) was treated with 3M aqueous methanolic trifluoroacetic acid to pH 1.0. The organic phase was extracted with dichloromethane (100cm^3) and washed with brine (60cm^3) and water (60cm^3) and then dried over MgSO_4 . Removal of solvent left a yellow oil. 6.4g, 95%.

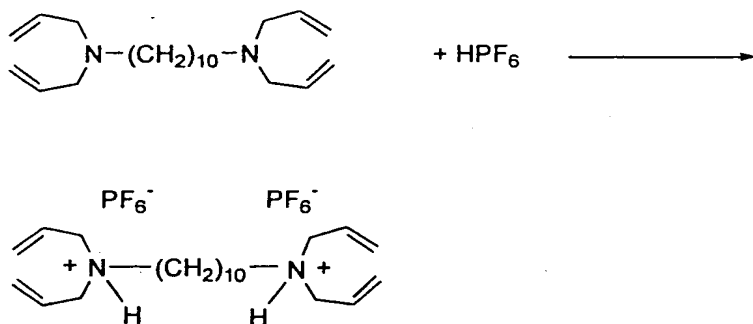
$^1\text{HNMR}$ (CDCl_3) δ : 1.30(m, 12H), 1.65(quin, 4H), 3.0(quin, 4H), 3.72(s, 8H), 5.60 (m, 8H), 5.90(m, 4H), 10.10(s, 2H).

Ir v max (KCl disc): 2934, 2861, 1780, 1669, 1428, 1169.3(s), 994.5, 950.8, 798, 722, 706, 617cm^{-1}

Step 3

The monomer from step 2 above (0.2g) and Irgacure 184 (5mg) were dissolved in dry dichloromethane (2cm³) and the solution was spread evenly on a 18 x 25 cm glass plate. The solvent was evaporated off to leave a thin film. It was then irradiated with a Philips UVA sunlamp (75w) for 10 minutes. The resultant cross-linked polymer was removed as strips (scalpel), washed in dichloromethane (50 cm³) and thoroughly dried. Yield 0.1g, 50%.

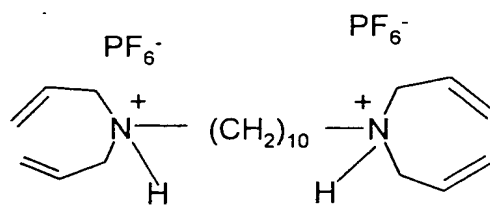
Ir v_{max} (KCl disc): 2940, 2864, 1780, 1650, 1428, 1170, 995, 951, 799, 743, 722, 620cm⁻¹

Example 2Step 1

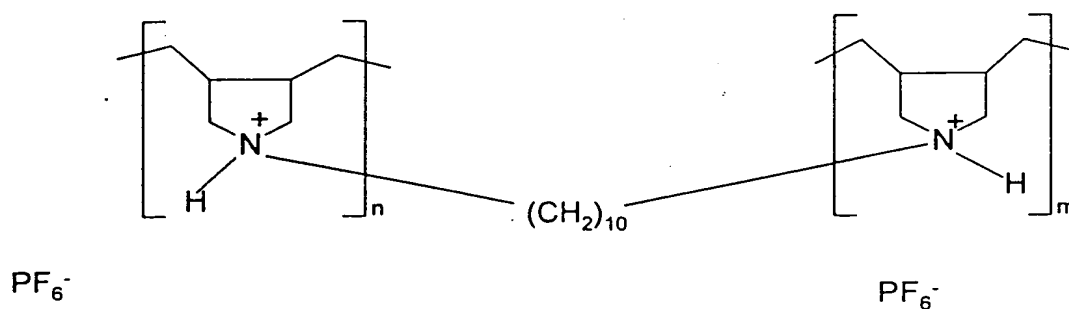
The monomer obtained in Example 1 step 1 (5.0g) was treated with a 3M aqueous methanolic solution of hexafluorophosphonic acid (3.0m) to pH1. The PF_6^- salt was extracted using dichloromethane ($2 \times 100\text{cm}^3$) and the combined extracts were dried over MgSO_4 . Removal of solvent left a yellow oil. 9.16g, 96%.

Ir v max (KCl disc): 3508, 3199, 2931, 2859, 2663, 1691, 1648, 1469, 1427, 1290, 1142, 1049, 996, 953, 842.6(s), 737 cm^{-1} .

^1H NMR (CDCl_3) δ . 1.25(s, br, 12H), 1.65(s, br, 4H), 2.95(s, br, 4H), 3.65(s, br, 8H), 5.60 (m, 8H), 5.90 (m, 4H), 9.75(s, br, 2H)

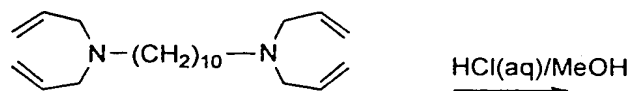
Step 2

hv/Irg 184



The monomer from step 1 (0.2g) was dissolved with Irgacure 184 (5mg) in dry dichloromethane (1.0cm³) and the solution spread evenly on a 2 x 4 sq" sheet of aluminium. The solvent was removed by warming and the film was irradiated with the Philips UVA (75w) u/v lamp for 10 minutes to form a cross-linked polymeric coating.

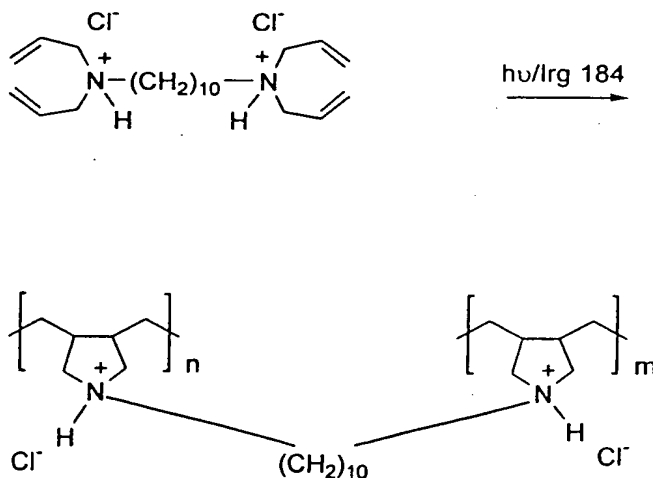
IRU max. 3434, 2937, 2859, 2717, 1674, 1467, 1297, 1140, 843(s) (P-F), 558cm⁻¹

Example 3Step 1

The monomer from Example 1 step 1 (1.0g), was treated with 3M aqueous methanolic hydrochloric acid to pH 1.0 (universal indicator paper). The organic phase was extracted with dichloromethane (100cm³) and washed with brine (60cm³) then water (60cm³) and dried over MgSO₄. Removal of solvent left a heavy yellow oil. 1.2g, 96%.

Ir v max (KCl. Disc): 2929, 2855, 2632, 2536, 1645, 1456, 1426, 1362, 1222, 997, 948cm⁻¹

¹HNMR (DMSO)δ: 1.25(m, 10H), 1.67(m, 4H), 2.89(m, 4H), 3.66(s, 8H), 5.42-5.53(m, 8H), 5.96-6.01(m, 4H), 11.20(s, 2H).

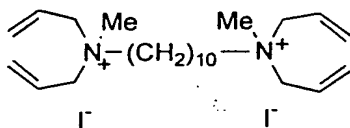
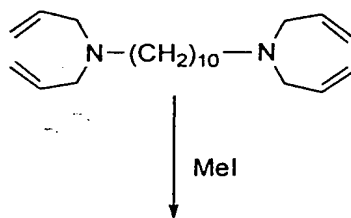
Step 2

The diallylamine salt obtained in step 1 above (1.0g, 0.0025mol) and Irgacure 184 (25.3mg, 0.000124mol) were dissolved in dry dichloromethane (2 cm³) and the solution spread on an 18 x 25 cm² glass plate. The solvent was allowed to evaporate and the remaining clear film was irradiated for approximately 3 minutes under a Philips UVA (75w) sunlamp. The resultant cross-linked polymer was removed from the glass plate, washed in dichloromethane and. Yield 0.75g, 75%.

Ir v max (KCl disc): 2800-2200 (broad), 1620(w), 1455(s), 1050(w), 1000(w), 950(w), 720(w) cm⁻¹

Example 4

Step 1



The monomer obtained as described in Example 1 step 1 (3.0g, 0.0094mol) and methyl iodide (2.60g, 0.22mol) in dry dichloromethane (30cm³) were refluxed together for 7 hours. The solvent and residual methyl iodide were removed in vacuo and the orange residue re-dissolved in dry dichloromethane (100cm³). The orange solution was washed in brine (50cm³) and dried over MgSO₄. Removal of solvent gave an orange oil which formed a soft solid on standing. Yield 4.95g, 89%.

$^1\text{H NMR}$ (DMSO) δ : 1.27 (m, 12H), 1.69 (m, 4H), 2.99 (6H), 3.10-3.20 (m, 4H), 3.95 (d, 8H), 5.55-5.75 (m, 8H), 5.95-6.18 (m, 4H).

Ir v max (KCl disc): 3081, 2925, 2854, 2361, 1689, 1641, 1470, 1424, 1371, 1302, 1246, 994, 943, 894, 868, 724, 668.

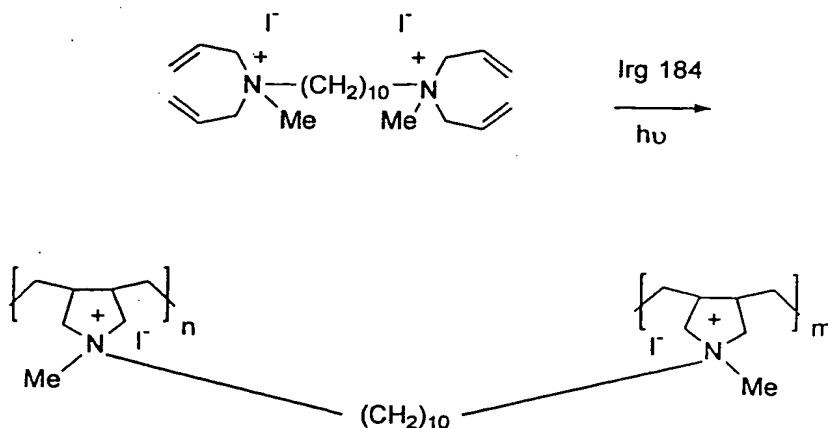
Step 1A

In an alternative preparation of the compound of step 1 above, the monomer obtained as described in Example 1 step 1 above (10.0g, 0.030mol) and methyl iodide (9.23g, 0.065mol) in a mixture of tetrahydrofuran (100cm³) and dichloromethane (20cm³) were stirred together. After 0.5 hours the solution began to become turbid and the turbidity increased as time progressed. The solvent was removed in vacuo and the white solid residue was suspended in 40/60 petrol (100 cm³) and stirred for 1 hour. Filtration and thorough drying in vacuo gave 17.79g, 96% of white, soft solid.

$^1\text{H NMR}$ (CDCl₃) δ : 1.20-1.40 (s, 12H), 1.80 (s, 4H), 3.20 (s, 6H), 3.40 (m, 4H), 4.15 (m, 8H), 5.65-5.86 (m, 8H), 5.95-6.10 (m, 4H)

Ir v max (KCl disc): 3080, 3050, 2930, 2860, 1640, 1470, 1440, 1425, 1370, 1300, 995, 945 cm⁻¹

Step 2



The monomer from step 1 above (0.7g, 0.00114mol) and Irgacure 184 (23.2mg, 0.00014mol) were dissolved in dry dichloromethane (3cm³). The monomer/photoinitiator mixture was spread evenly on an 18 x 25 cm³ glass plate and the solvent left to evaporate in air to leave a clear, light yellow film. The film was irradiated with a Philips UVA (75w) sunlamp for 15 minutes. Examination showed that the monomer had polymerised to form a hard, cross-linked polymer. The polymer was removed as strips of clear film and placed in dry dichloromethane (100cm³) and the mixture stirred for 15 minutes. The film strips were removed by filtration and dried in vacuo.

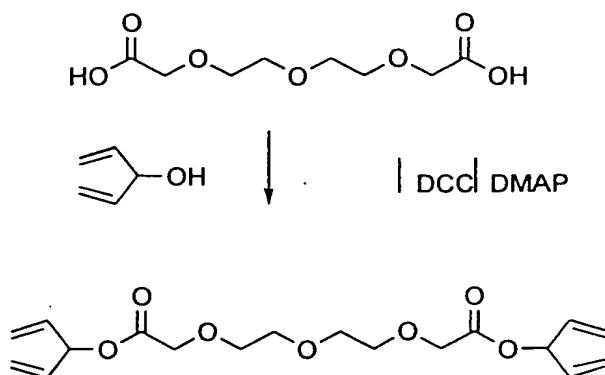
Ir v max (KCl disc): 2923, 2852, 1680(w), 1613, 1461(s), 950(s), 726cm⁻¹.

A similar reaction using 1.0g(0.0016mol) of the monomer obtained in step 1A above and 16.3g (0.00008mol) Irgacure 184 produced 0.84g (84%) of cross-linked polymer.

Ir v max (KCl disc): 3480 (H₂O), 2920, 2860, 1640(w), 1460, 1000, 955 cm⁻¹

Example 5

Step 1

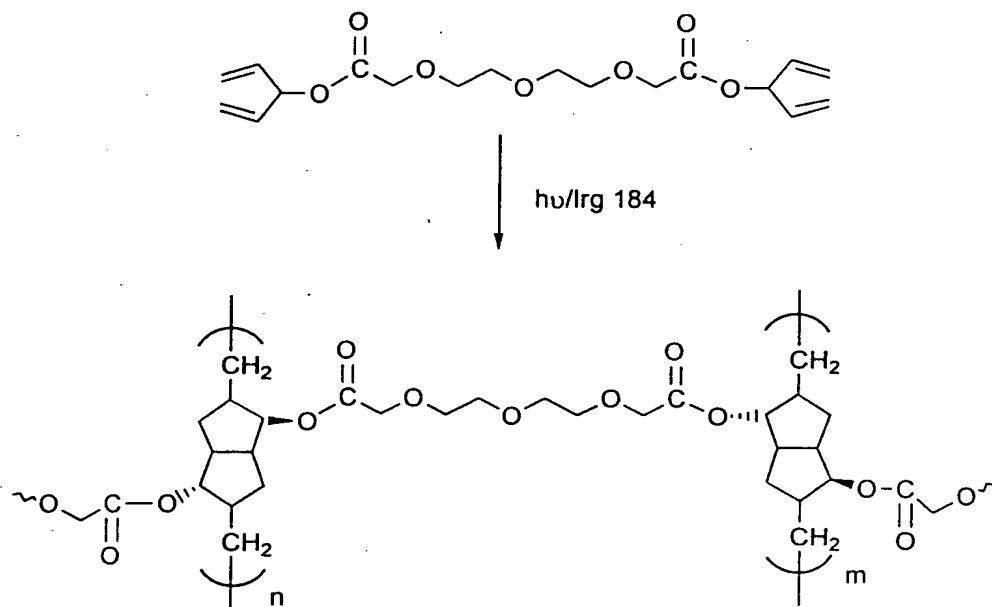


3,6,9-Trioxaundecandioic Acid (4.4g, 0.0179 mol), 1,4-pentadien-3-ol (3.0g, 0.0357 mol), 1,3-dicyclohexylcarbodiimide (7.63g, 0.037 mol) and 4-dimethylaminopyridine (250 mg) were stirred together in dry dichloromethane (100 cm³) for 48 hours at room temperature. The 1,3-dicyclohexylurea was removed by filtration and the solvent removed in vacuo to leave an oil. Purification using silica gel and ethyl acetate - 40:60 petrol (1:1) as eluent followed by removal of solvent and thorough drying gave 6.4g, 91% of colourless, clear oil.

Ir v max(thin film): 2920, 2860, 1750, 1635, 1420, 1380, 1350, 1270, 1250, 1195, 1150, 1120, 990, 935, 880, 850, 730, 690, 580 cm⁻¹

¹HNMR (CDCl₃)δ: 3.65-3.80(m, 8H), 4.15(s, 4H), 5.25-5.50(m, 10H), 5.75-5.95(m, 4H).

Step 2



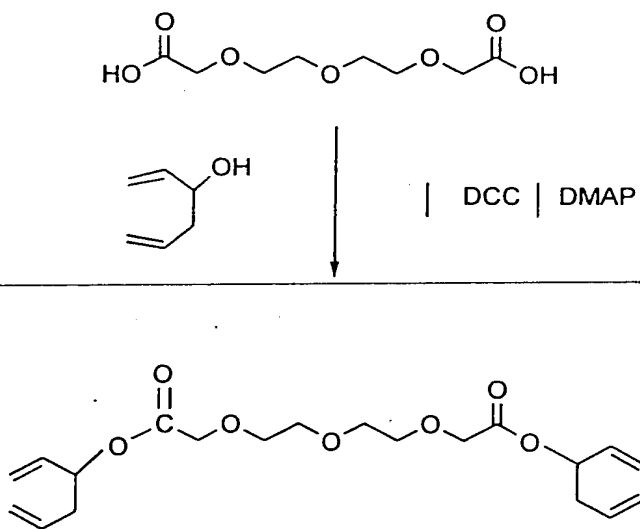
The monomer from Example 5 step 1 (1.5g, 0.0042mol) and Irgacure 184 (43mg) were dissolved in dry dichloromethane (2 ml) and the solution was spread evenly on an 18 x 25 cm plate

glass sheet. The solvent was allowed to dry in air then the remaining polymer/photoinitiator film was irradiated beneath a Philips UVA (70w) U/V sunlamp for 2 hours. The resultant cross-linked polymer was scraped (scalpel) from the plate and suspended in dry dichloromethane (20ml) and the suspension was stirred for approximately 15 minutes. The polymer was recovered by filtration and the retained solid washed with dry dichloromethane ($2 \times 10 \text{ cm}^3$) and then dried thoroughly to leave 0.6g 40% of clear film polymeric material.

Ir v max (thin film): 2920, 2860, 1740, 1630, 1450, 1380, 1275, 1200, 1145, 1120, 850 cm^{-1}

Example 6

Step 1



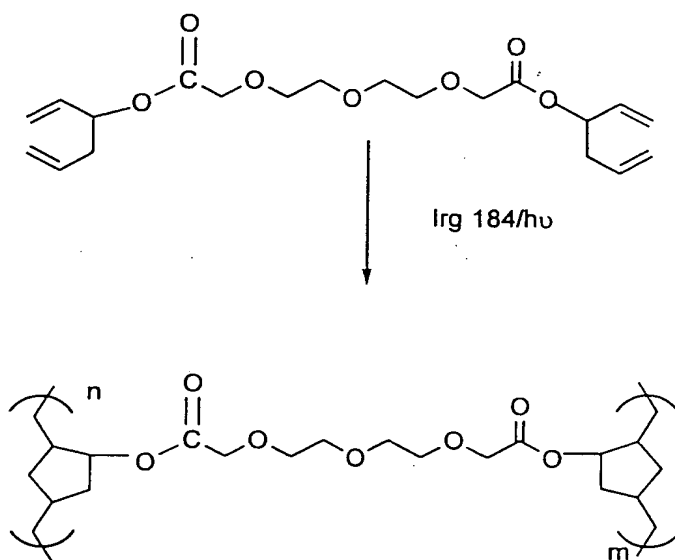
3,6,9-Trioxaundecandioic acid (5.33g, 0.024 mol), 1,5-Hexadien-3-ol (5.0g, 0.051 mol), 1,3-dicyclohexylcarbodiimide (10.5g, 0.051 mol) and 4-dimethylaminopyridine (250mg) were stirred together in dry dichloromethane (50 cm^3) at room temperature for 6 hours. The 1,3-dicyclohexylurea was removed by filtration and the solvent removed in vacuo to leave a

yellow oil which was purified by column chromatography using silica gel/ethyl acetate. Yield 8.0g, 87%.

$^1\text{H NMR}$ (CDCl_3) δ : 2.4 (t, 4H), 3.65 (m, 8H), 4.20 (s, 4H), 5.05-5.45 (m, 10H), 5.65-5.90 (m, 4H)

Ir v max (thin film): 2920, 2860, 1760, 1640, 1425, 1200, 1150, 1120, 990, 920 cm^{-1}

Step 2

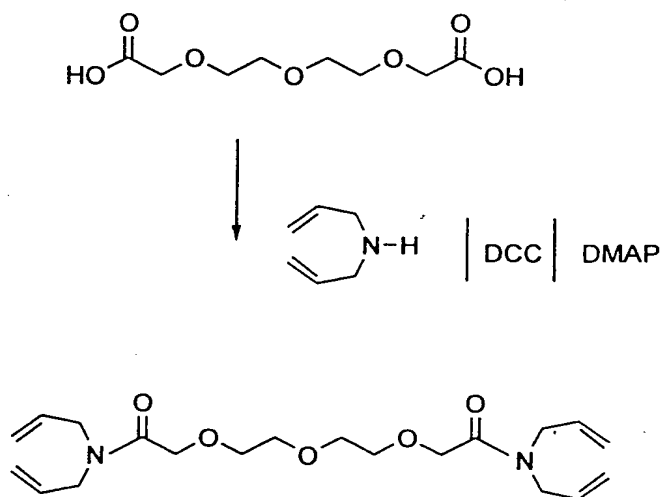


The monomer from step 1 above (1.6g, 0.0042mol) and Irgacure 184 (43mg, 5 mol%) were dissolved in dry dichloromethane (2 ml) and the solution was spread evenly on an 18 x 25 cm plate glass sheet. The solvent was allowed to dry in air then the remaining polymer/photoinitiator film was irradiated beneath a Philips UVA (70w) U/V sunlamp for 2 hours. The resultant cross-linked polymer was scraped (scalpel) from the plate and suspended in dry dichloromethane (20ml) and the suspension was stirred for approximately 15 minutes. The polymer was recovered by filtration and the retained solid washed with dry dichloromethane (2 x 10 cm^3) and then dried thoroughly to leave a clear film polymeric material. Yield 1.34g, 87%.

Ir v max (thin film): AWH/11: 2920, 2860, 1740(S), 1635, 1450, 1430, 1380, 1280, 1200, 1145, 1120, 990, 925, 850 CM-1

Example 7

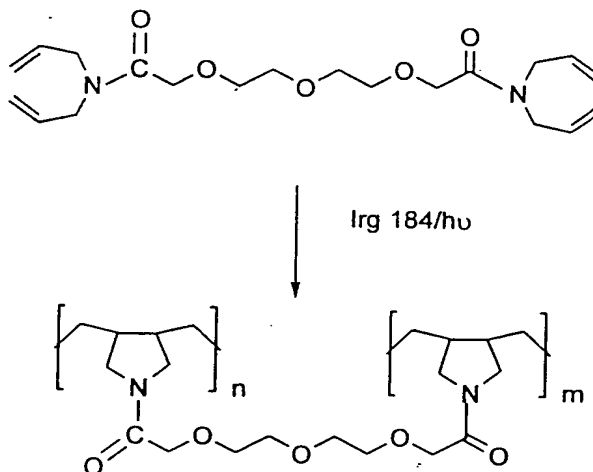
Step 1



3,6,9-Trioxaundecanoic acid (5.0g, 0.026 mol), diallylamine (5.10g, 0.055 mol), 1,3-Dicyclohexylcarbodiimide (11.35g, 0.055 mol) and 4-dimethylaminopyridine (0.5g) were stirred together in dry dichloromethane (100cm³) for 6 hours. The resultant 1,3-dicyclohexylurea was removed by filtration and the solvent removed in vacuo to give a yellow oil. Column chromatography using ethyl acetate - petrol 40/60 (1:1) followed by removal of solvent in vacuo and thorough drying gave the product as a yellow oil. (Yield 8.0g, 94%)

Ir v max (thin film): 2930, 2860, 1660(s), 1530, 1470, 1450, 1420, 1350, 1280, 1230, 1195, 1115(s), 995, 930, 755 cm⁻¹

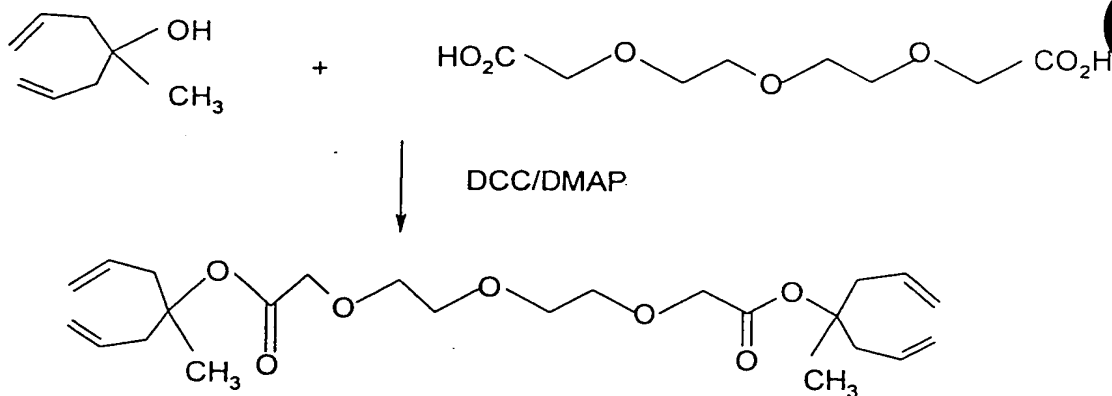
¹HNMR (CDCl₃)δ: 3.70(m, 8H), 3.90(m, 4H), 4.0(m, 4H), 4.25(s, 4H), 5.10-5.25(m, 8H), 5.75-5.90(m, 4H)

Step 2

Monomer from step 1 above (1.0g, 0.00263mol) and 5 mol% Irgacure 184 (27mg, 0.00013mol) were dissolved in dry dichloromethane (3cm³) and the solution spread over an 18 x 25 cm glass plate. The solvent was allowed to evaporate to leave a thin clear film. The film was then irradiated with a Philips UVA sunlamp (75w) for approximately 5 minutes to form a hard polymeric cross-linked coating. The coating was removed and washed in dry dichloromethane and then thoroughly dried (Yield 0.73g, 73%)

IRu (KCl disc) max: 2920, 2860, 1640(s), 1530, 1450, 1240, 1115(s), 730cm⁻¹

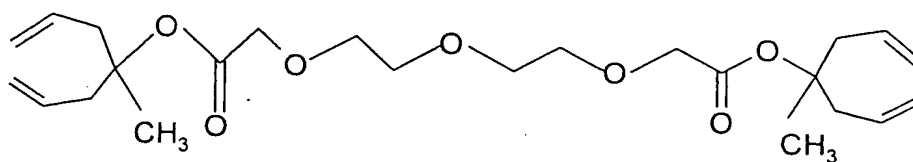
Example 8Step 1



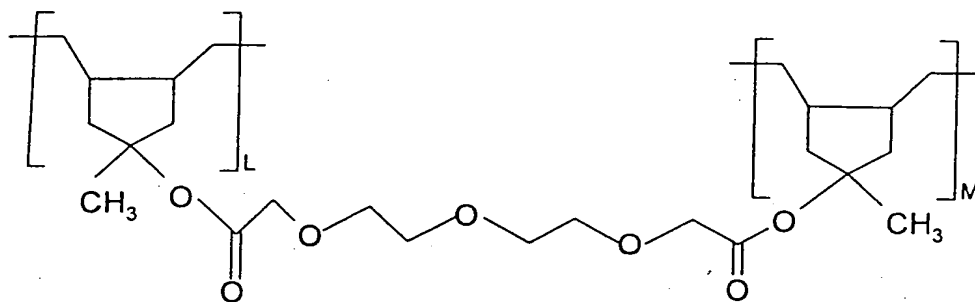
3,6,9-Trioxaundecandioic acid (2.64g, 0.012 mol), 1,1-diallylethanol (3.0g, 0.023 mol), 1,3-dicyclohexylcarbodiimide (5.16g, 0.025 mol) and 4-dimethylaminopyridine (150mg) were dissolved in dry dichloromethane (100 cm³) and the solution stirred for 18h at room temperature. 1,3-Dicyclohexylurea was removed by filtration and the solvent removed in vacuo to leave a yellow oil. Column chromatography using silica gel and ethyl acetate gave, after removal of solvent in vacuo, a clear oil, 4.9g, 94%.

¹HNMR (CDCl₃) δ 1.45 (s, 8H), 2.50-2.70 (m, A:B, 8H), 3.70 (s, 6H), 4.05 (s, 4H), 5.05-5.15 (m, 8H), 5.70-5.90 (m, 4H)

Ir v max (thin film): 2920, 2870, 1750, 1450, 1380, 1210, 1150, 1120, 740, 700 cm⁻¹

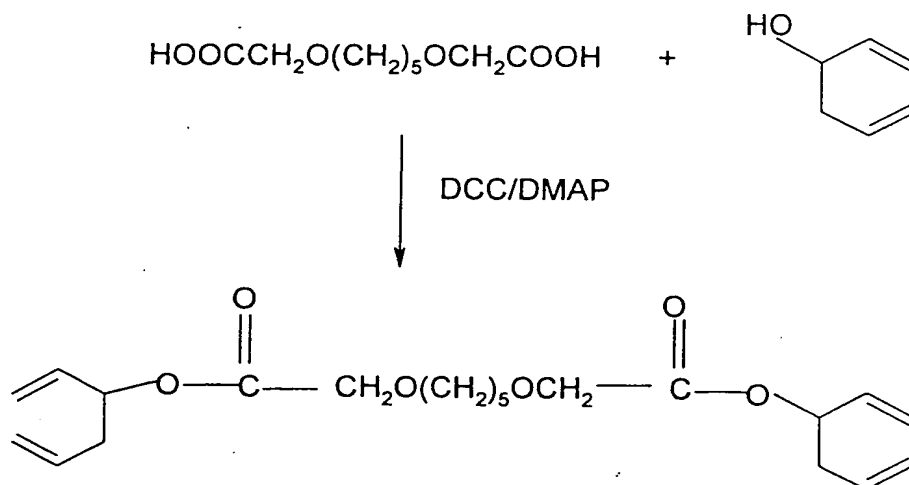
Step 2

hv/Irg 184



The monomer from Step 1 above (1.0g, 0.0023 mol) and Irgacure 184 (5 mol %; 23.5mg, 0.00012 mol) were dissolved in dry dichloromethane (3 cm³) and the solution spread over a 18 x 25 cm glass plate. The solvent was allowed to evaporate to leave a thin clear film. The film was then irradiated with a Philips UVA sunlamp (75 w) to form a hard cross-linked polymer coating. The coating was removed and washed in dry dichloromethane and then dried thoroughly. Yield 0.78g, 78%.

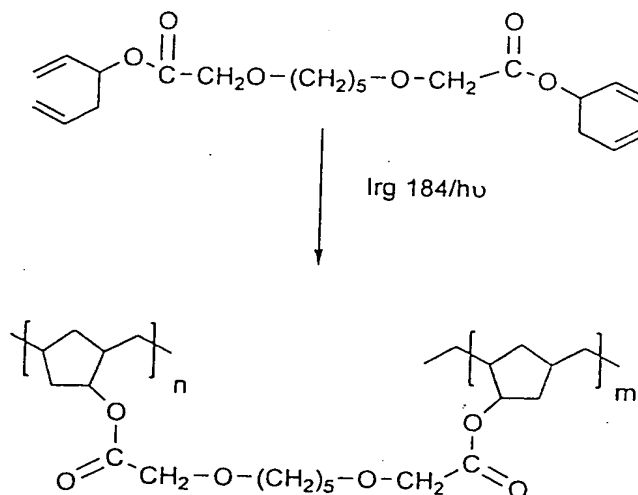
IR ν max (KCl disc): 2940, 2880, 1750, 1450, 1380, 1205, 1145, 1120, 1030, 960 cm⁻¹

Example 9Step 1

The diacid A above (2.5g, 0.0114 mol), 1,5-hexadien-3-ol (1.34g, 0.024 mol), 1,3-dicyclohexylcarbodiimide (206.33) (5.16g, 0.025 mol) and 4-dimethylaminopyridine (200mg) were placed in dry dichloromethane (100cm³) and the solution stirred for 18 hours at room temperature. 1,3-dicyclohexylurea was removed by filtration and the solvent removed in vacuo to leave a yellow oil. Column chromatography using silica gel with ethyl acetate gave a clear oil, 2.84g, 66%.

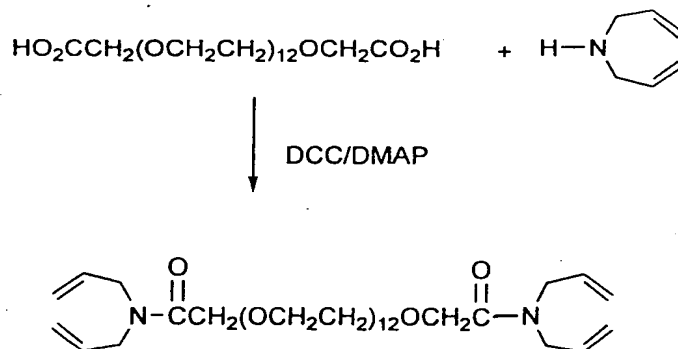
¹HNMR (CDCl₃) δ 1.20(quin, 2H), 1.65 (m 4H), 2.40(t, 4H), 3.60 (d, 4H), 4.20 (s, 4H), 5.05-5.45 (m, 10H), 5.65-5.90 (m, 4H).

Ir v max (thin film): 2920, 2860, 1750, 1700, 1510, 1430, 1240, 1200, 1140, 1030, 990, 920, 760cm⁻¹

Step 2

Monomer from step 1 above (0.7g, 0.001894 mol) and Irgacure 184 (37.6mg, 0.0000184 mol) were dissolved in dry dichloromethane (3cm³) and the solution was spread on an 18 x 25 cm³ glass plate. The solvent was allowed to evaporate to leave a clear film. This was irradiated with a Philips UVA (75w) sunlamp for 2 hours until the film hardened. The film was removed and placed in dry dichloromethane (50cm³) and stirred for 1 hour. The cross-linked polymer was removed by filtration and washed with dry dichloromethane (2 x 50 cm³) and dried thoroughly to leave a creamy coloured polymeric solid. Yield 0.35g, 50%.

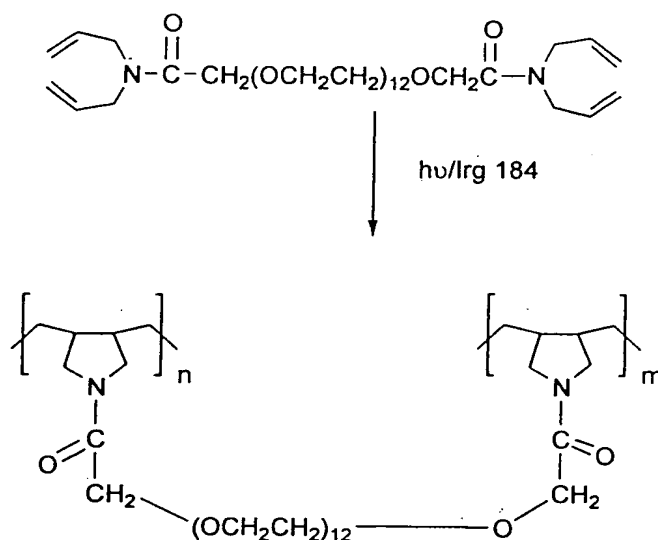
Ir v max (KCl disc): 2940, 2860, 1750(s), 1450, 1285, 1205, 1130, 1030cm⁻¹

Example 10Step 1

Polyethylene glycol 600 diacid (12.0g, 0.020 mol), diallylamine (4.67g, 0.048 mol), 1,3-dicyclohexylcarbodiimide (10.6g, 0.048 mol) and 4-dimethylaminopyridine (600mg) were placed in dichloromethane (100 cm³) and the mixture stirred for 24 hours at room temperature. The 1,3-dicyclohexylurea was removed by filtration and the solvent removed in vacuo to leave a yellow oil. Column chromatography (silica gel/ethyl acetate) followed by removal of solvent in vacuo gave a pale yellow oil. 13.90g, 92%.

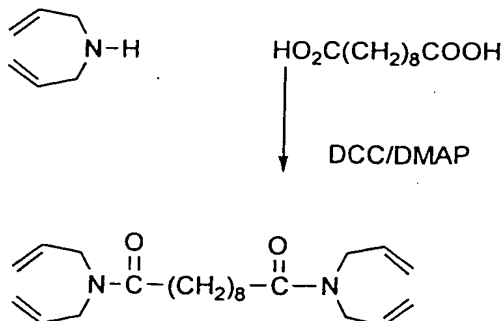
¹HNMR (CDCl₃)δ: 3.60(m, 48H), 3.90(d, 4H), 4.0(d, 4H), 4.20(s, 4H), 5.15(m, 8H), 5.75(m, 4H)

Ir v max(thin film): 3016, 2922, 1662(s), 1470, 1353, 1219, 1114, 931, 756, 666 cm⁻¹

Step 2

Monomer from Step 1 (1.0g) and Irgacure (1.5mg) were dissolved in dry dichloromethane (3 cm³) and thoroughly mixed. The solution was spread evenly on an 18 x 25 cm glass plate and the solvent allowed to evaporate to leave a thin film of monomer. The film was irradiated with the Philips UVA (75w) sunlamp for 30 minutes to form a soft, permeable to water, cross-linked polymer film.

Ir v max (thin film): 3438, 2946, 2371, 1703, 1648(s), 1544, 1510, 1457, 1352, 1099(vs), 953, 856, 727, 551 cm⁻¹

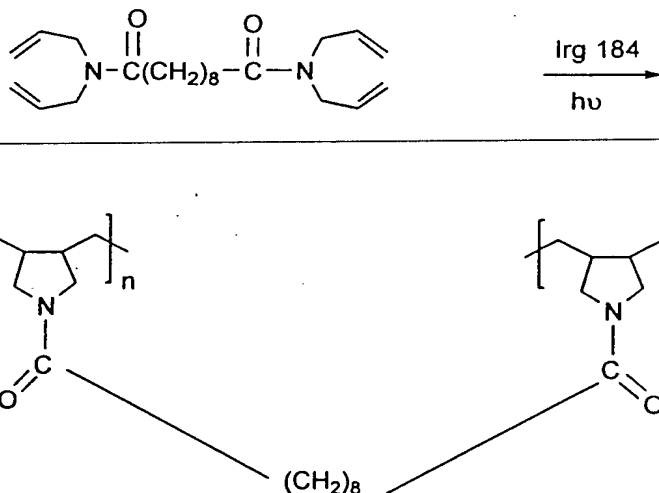
Example 11Step 1

Diallylamine (9.72g, 0.1 mol), Sebacic acid (10.00g, 0.0050 mol), 1,3-dicyclohexylcarbodiimide (22.70g, 0.11 mol) and 4-dimethylaminopyridine (0.450g) were stirred together in dry dichloromethane (100cm³) for 6 hours. The resultant 1,3-dicyclohexylurea was removed by filtration and the solvent removed in vacuo to give a yellow oil. Column chromatography using ethyl acetate - petrol 40/60 (1:1) followed by removal of solvent in vacuo and thorough drying gave the product as a yellow oil. 15.90g, 90%.

Ir v(thin film) max: 2920, 2850, 1690(w), 1640(s), 1520, 1460, 1410, 1220, 990, 920, 730cm⁻¹

¹HNMR (CDCl₃)δ: 1.10-1.45 (m, 6H), 1.50-2.00 (m, 6H), 2.40 (t, 4H), 3.90 (d, 4H), 4.0 (d, 4H), 5.05-5.20 (m, 8H), 5.20-5.90 (m, 4H)

Step 2

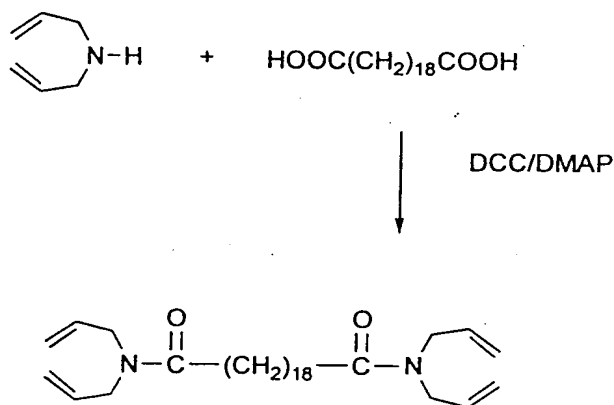


Monomer from Step 1 (1.00g, 0.0028 mol) and Irgacure 184 (28.3 mg, 0.000139 mol) were dissolved in dry dichloromethane (3cm³) and the solution spread over a 18 x 25 cm glass plate. The solvent was allowed to evaporate to leave a thin clear film.

The film was then irradiated with a Philips UVA sunlamp (75w) for approximately 5 minutes to form a hard polymeric cross-linked coating. The coating was removed and washed in dry dichloromethane and then thoroughly dried. Yield 0.80 g, 80%.
 Ir v max KCl disc): 2920, 2860, 1640, 1530, 1450, 1230(w), 1340(w), 1230(w), 1000(w), 930(w).

Example 12

Step 1

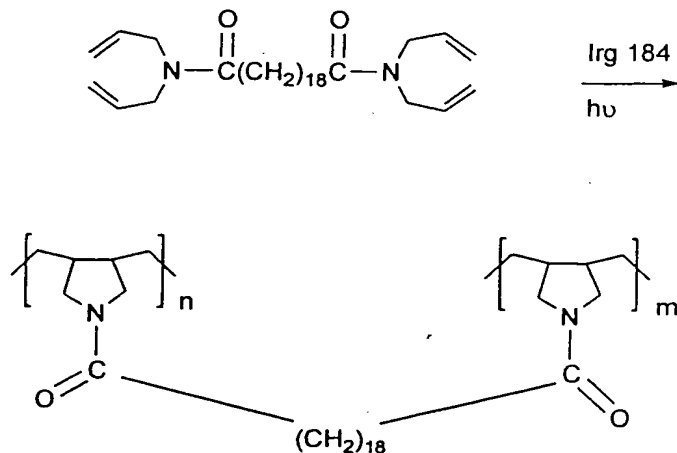


Eicosanedioic acid (5.0g, 0.0146 mol), diallylamine (3.12g, 0.032 mol), 1,3-dicyclohexylcarbodiimide (6.60g, 0.032 mol) and 4-dimethylaminopyridine (200mg) were dissolved in dichloromethane/tetrahydrofuran mixture (1:1) (100 cm³) and the mixture stirred at room temperature for 72 hours. 1,3-Dicyclohexylurea was removed by filtration and the solvent removed in vacuo to leave a yellow oil. Column chromatography using silica gel/ethyl acetate followed by removal of solvent in vacuo and thorough drying gave a pale yellow oil. 6.35g, 87%.

¹HNMR (CDCl₃)δ: 1.20(s, br, 28H), 1.60(m, 4H), 1.80(m, 4H), 3.90(d, 4H), 4.0(d, 4H), 5.10(m, 8H), 5.75(m, 4H).

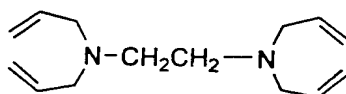
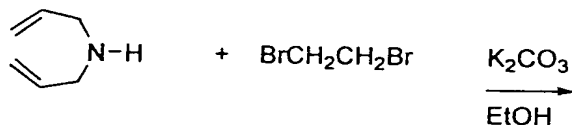
Ir v max (thin film): 3006, 2927, 2854, 1643, 1530, 1466, 1415
1217, 1084, 992, 925, 893, 756, 666 cm^{-1} .

Step 2



Monomer from Step 1 (0.25g) and Irgacure 184 (5mg) were dissolved in dry dichloromethane (1.0 cm^3) and the solution was heated (water bath) to ensure even distribution of photoinitiator. The solution was spread evenly on a 4 x 2" piece of aluminium foil and the solvent was allowed to evaporate off to leave a thin film of monomer/photoinitiator. This was irradiated with a Philips UVA (75w) sunlamp for 30 minutes until a hard cross-linked polymer was formed. To test for hydrophobicity, the foil + polymer was subjected to running water for 30 minutes. After this time the polymer laminate was not adversely affected, i.e. no loss of adhesion to the foil.

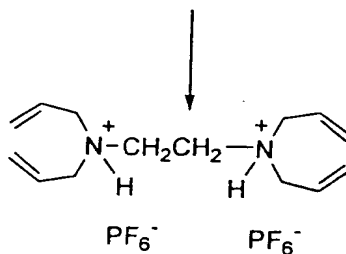
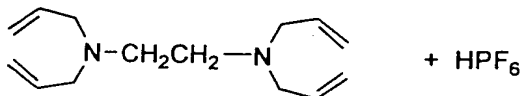
Ir v max (KCl disc): 2924, 2851, 1648, 1534, 1452, 1227, 721 cm^{-1}

Example 13Step 1

Diallylamine (12.90g, 0.132 mol), 1,2-dibromoethane (12.40g, 0.066 mol) and potassium carbonate (18.80g, 0.132 mol) were refluxed in ethanol (100cm³) for 24 hours. Solids were removed by filtration and solvents removed in vacuo to leave a yellow oil. The oil was purified by column chromatography (silica gel/ethyl acetate) to leave a pale yellow oil. 13.40, 92%.

¹HNMR (CDCl₃)δ: 2.55(s, 4H), 3.10(d, 8H), 5.10(m, 8H), 5.80(m, 4H)

Ir v max (thin film): 3082, 3012, 2983, 2927, 2806, 1645, 1447, 1420, 1355, 1262, 1109, 997, 919, 559 cm⁻¹

Step 2

Monomer from Step 1 (5.0g) was treated with an aqueous methanolic solution of hexafluorophosphonic acid 60% solution in H₂O (3.0m) to pH1. The PF₆⁻ salt was extracted using dichloromethane (2 x 100cm³) and the combined extracts were dried over MgSO₄. Removal of solvent left a yellow oil. 8.0g, 96%.

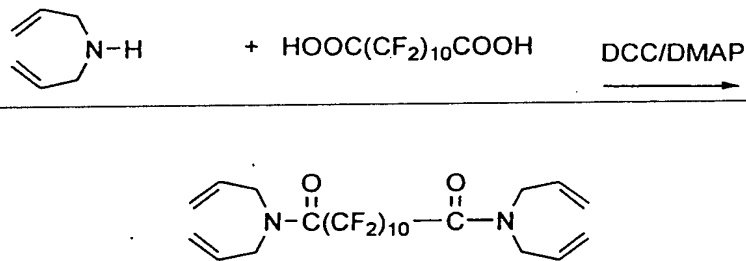
¹HNMR(CDCl₃)δ: 3.60(d, 2H), 3.75(d, 2H), 3.80(s, 8H), 5.55(m, 8H), 5.90(m, 4H), 9.80(s, br, 2H)

Ir v max (thin film): 3428, 2986, 2634, 1460, 1426, 1294, 1246, 1142, 1053, 977, 953, 842, 740 cm⁻¹

The product may then be polymerised, for example as described in Example 1 Step 3 above.

Example 14

Step 1

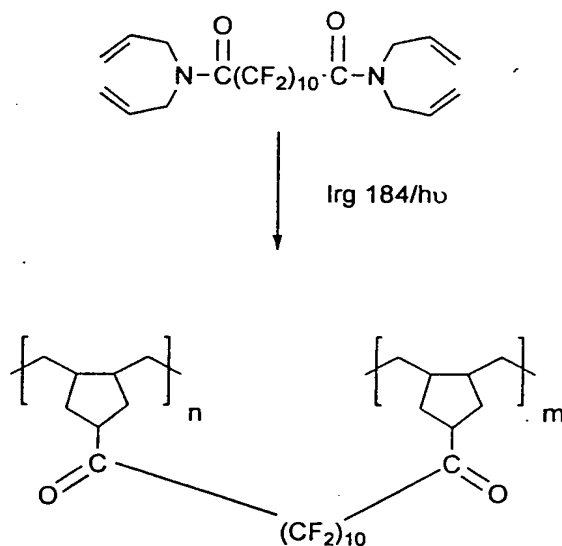


Diallylamine (1.41g, 0.0145 mol), perfluoro-1,10-decanedicarboxylic acid (2.5g, 0.0073 mol), 1,3-dicyclohexylcarbodiimide (3.20g, 0.0155 mol) and 4-dimethylaminopyridine (0.5g) were stirred together in dry dichloromethane (60 cm³) for 6 hours. The solvent was removed in vacuo to leave a white solid which was purified using column chromatography (ethyl acetate-petrol 40/60 1:1) and dried thoroughly to give 2.96g, 79% of clear oil.

$^1\text{H NMR}$ (CDCl_3) δ : 3.90 (d, 4H), 4.00 (d, 4H), 5.10-5.25 (m, 8H), 5.70-5.81 (m, 4H)

Ir v max (thin film): 2933, 2857, 1692, 1645.5, 1611.4, 1576, 1454, 1419, 1377, 1350, 1219, 1151, 1081, 992, 932, 892, 735, 657, 556.

Step 2

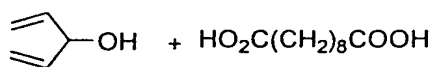


Monomer from Step 1 (1.0g, 0.0019 mol) was dissolved in dry dichloromethane (3 cm^3) and Irgacure 184 (20mg, 0.000095 mol) and the resultant solution spread evenly over an 18 x 25 cm glass plate. The solvent was allowed to evaporate off to leave a clear liquid layer of monomer/photoinitiator. The plate was placed under a Philips UVA (75w) sunlamp for approximately 15 minutes. The resultant clear film was removed (powdery) and dried after stirring for 30 minutes in dry dichloromethane (100 cm^3) to leave 0.79g, 79% of white powder.

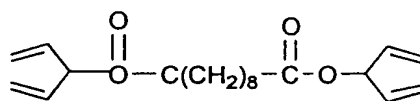
Ir v max (thin film): 2936, 2859, 1691, 1624, 1576, 1455, 1372, 1218, 1151, 1079, 892, 729, 654, 555 cm^{-1}

Example 15

Step 1



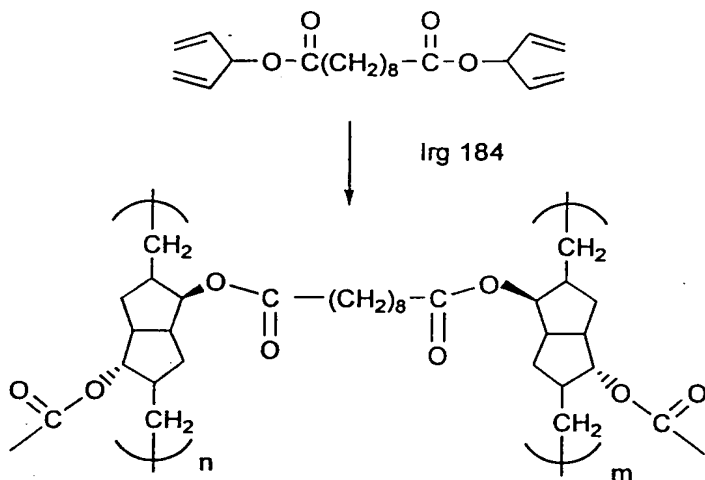
DCC/DMAP



Sebacic acid (2.0g, 0.0099 mol), 1,4-pentan-3-ol (1.7g, 0.02 mol), 1,3-dicyclohexylcarbodiimide (4.52g, 0.022 mol) and 4-dimethylaminopyridine (200g) in dry dichloromethane (60 cm^3) were stirred together for 18 hours. The 1,3-dicyclohexylurea was removed by filtration and solvent removed to leave clear oil. This was dissolved in 40/60 petrol (100 cm^3) and washed in water then dried over MgSO_4 . Removal of solvent left a clear, colourless oil which tlc (dichloromethane) (developing in iodine) showed as a single spot. The oil was thoroughly dried in vacuo to leave 2.49g, 75% of clear oil.

^1H NMR (CDCl_3) δ : 1.30(s, 8H), 1.60(t, 4H), 2.35(t, 4H), 5.15-5.35(m, 8H), 5.65-5.95(m, 6H)

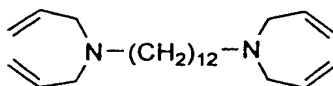
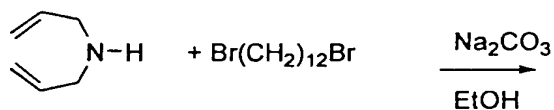
Ir v max (thin film): 2920, 2860, 1730, 1640, 1510, 1460, 1410, 1365, 1240, 1165, 1095, 985, 930 cm^{-1}

Step 2

Monomer from Step 1 (1.0g, 0.003 mol) and Irgacure 184 (31mg, 0.00015 mol) were dissolved in dry dichloromethane (2 ml) and the solution was spread evenly on an 18 x 25 cm plate glass sheet. The solvent was allowed to dry in air then the remaining polymer/photoinitiator film was irradiated beneath a Philips UVA (75w) sunlamp for 2 hours. The resultant cross-linked polymer was scraped (scalpel) from the plate and suspended in dry dichloromethane (20 ml) and the suspension was stirred for approximately 15 minutes. The polymer was recovered by filtration and the retained solid washed with dry dichloromethane (2 x 10 cm³) and then dried thoroughly to leave 0.85 of clear film polymeric material.

Yield 0.85g, 85%

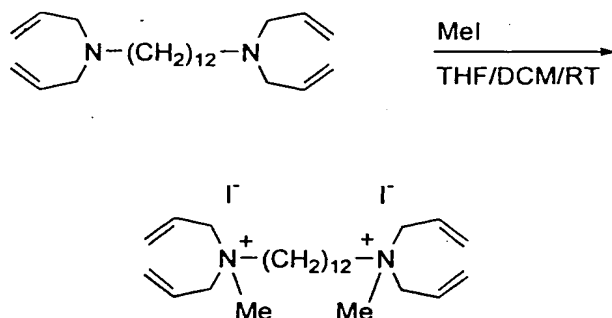
Ir v max (thin film): 2920, 2860, 1725, 1520, 1450, 1365, 1240, 1170, 1090, 985cm⁻¹

Example 16Step 1

Diallylamine (12.70g, 0.134 mol), 1,12-dibromododecane (20.0g, 0.061 mol) and potassium carbonate (18.50g, 0.134 mol) in ethanol (100cm³) were refluxed together for 18 hours. The solids were removed by filtration and the solvent removed in vacuo to leave a yellow oil. The oil was passed through a silica gel column using ethyl acetate as the eluent. Removal of solvent in vacuo gave a pale yellow oil which was thoroughly dried. Yield 17.4g, 79%.

¹HNMR (CDCl₃)δ: 1.20(m, 16H), 1.45(t, 4H), 2.40(t, 4H), 3.10(d, 8H), 5.05-5.15(m, 8H), 5.80(m, 4H)

Ir v max (thin film): 3080, 3020, 2920, 2860, 2800, 1645, 1470, 1420, 1355, 1260, 1155, 1115, 1090, 1000, 920, 725 cm⁻¹

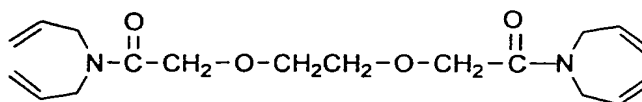
Step 2

The diamine from step 1 (10.00g, 0.028 mol) and methyl iodide (8.52g, 0.060 mol) in a mixture of tetrahydrofuran (100cm³) and dichloromethane (20cm³) were stirred together. After 0.5 hours the solution began to become turbid and the turbidity increased as time progressed. The solvent was removed in vacuo and the white solid residue was suspended in 40/60 petrol (100 cm³) and stirred for 1 hour. Filtration and thorough drying in vacuo gave 17.40g, 97% of white, soft solid.

¹HNMR (CD₂Cl₂)δ: 1.15-1.40(m, 16H), 1.80(s, br, 4H), 3.20(s, 6H), 3.30-3.45(m, 4H), 4.15(d, 8H), 5.65-5.90(m, 8H), 5.95-6.15(m, 4H)

Ir v max (thin film): 2920, 2860, 1690, 1640, 1470, 1370, 1300, 1250, 1000, 945 cm⁻¹

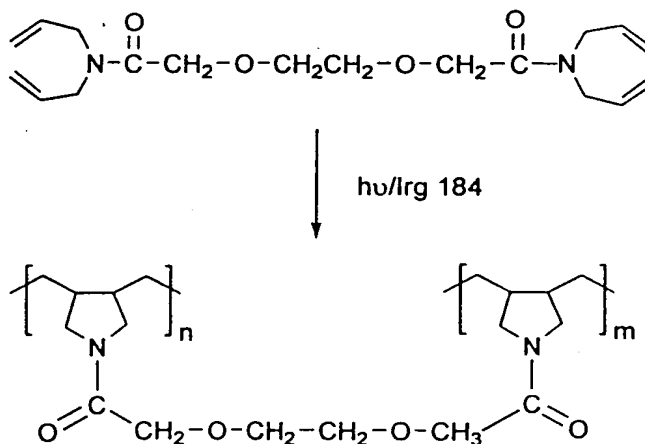
This material could be polymerised as described in previous examples.

Example 17Step 1

Diallylamine (8.80g, 0.0090 mol), 3,6-dioxaoctandioic acid (8.00g, 0.0448 mol) were mixed together as shown in Example 15 Step 1. The mixture was stirred in dichloromethane for 24 hours. The crude product was recovered and purified via silica gel/ethyl acetate to leave a clear oil. Yield 13.43g, 89%.

$^1\text{H NMR}$ (CDCl_3) δ : 3.70 (s, 4H), 3.80 (d, 4H), 3.95 (d, 4H), 4.20 (s, 4H), 5.20 (m, 8H), 5.60 (m, 4H)

Ir ν max (thin film): 3080, 2940, 2860, 1650, 1530, 1470, 1420, 1350, 1280, 1235, 1120, 995, 930, 860, 815 cm^{-1}

Step 2

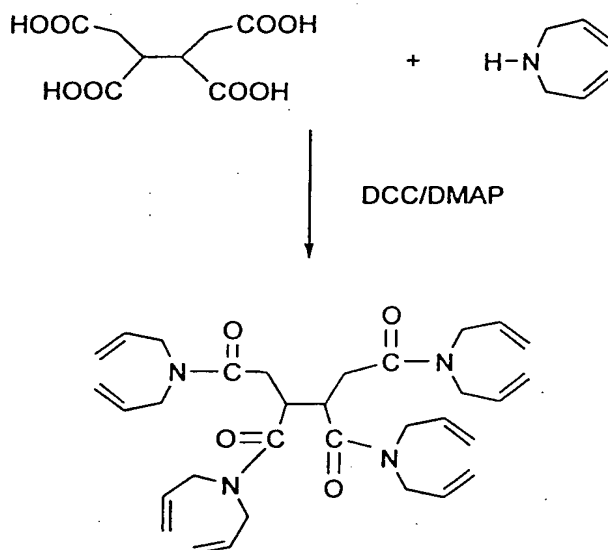
Irgacure 184 (5mg) as placed in Monomer from Step 1 (0.2g) and heated to form a clear solution. It was then stirred to

ensure complete mixing of photoinitiator then placed on a 1.5²in piece of copper (ex DRA) and spread evenly using 100 μ m K bar. It was then irradiated for 1 hour beneath a Philips UVA sunlamp and allowed to stand for 24 hours.

Ir v max (thin film): 2940, 2860, 1640 (strong), 1460, 1345, 1125, 730 cm^{-1}

Example 18

Step 1

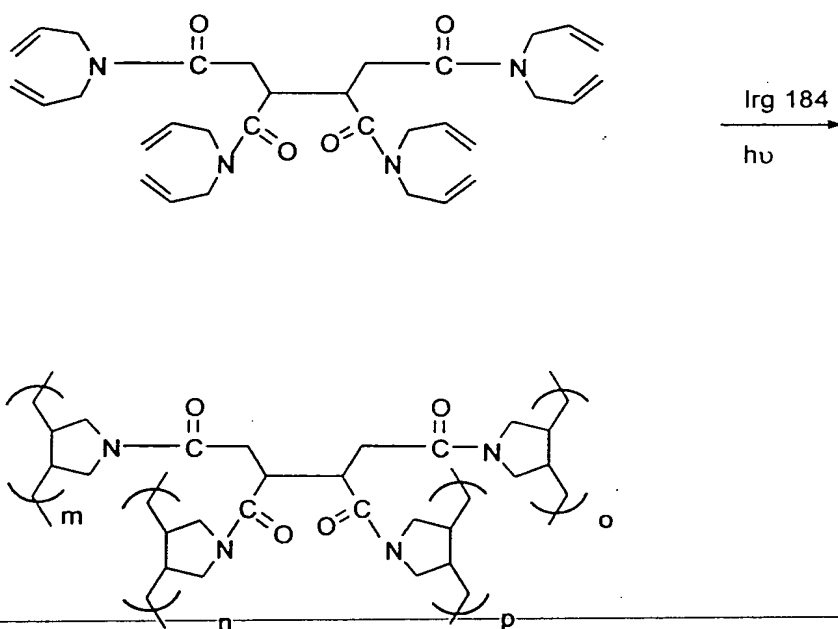


Meso-butan-1,2,3,4-tetracarboxylic acid (20.0g, 0.0428 mol), diallylamine (39.0g, 0.20 mol), 1,3-dicyclohexylcarbodiimide (82.50g, 0.20 mol) and 4-dimethylaminopyridine (2.0mg) were dissolved in dichloromethane/tetrahydrofuran (1:1) mixture (200 cm³) and the mixture was stirred at room temperature for 120 hours. 1,3-dicyclohexylurea was removed by filtration and the solvent removed in vacuo to leave a yellow oil. Column chromatography (silica gel/ethyl acetate) followed by removal of solvent in vacuo gave a heavy pale yellow oil which solidified on standing. 42.3g, 89%.

$^1\text{H NMR}$ (CDCl_3) δ : 2.90 (m, 4H), 3.50 (m, 2H), 3.80 (m, 16H), 5.20 (m, 16H), 5.70 (m, 8H)

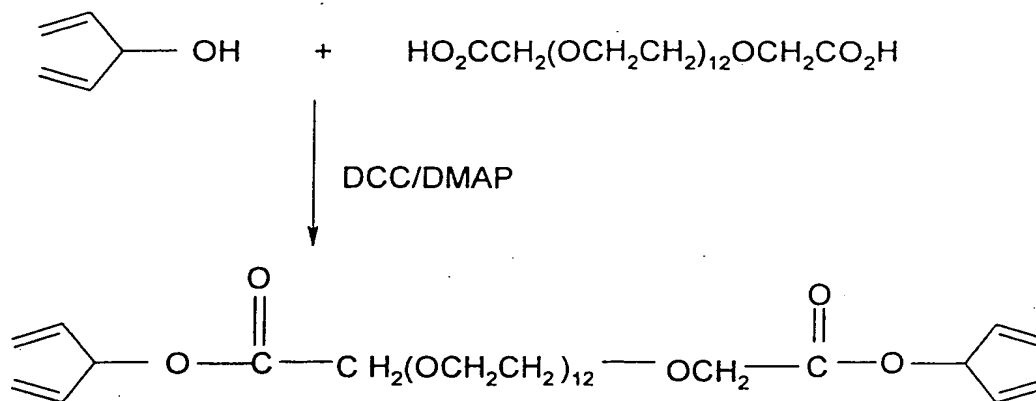
Ir v max (thin film): 3323, 3086, 2935, 2861, 1650, 1545, 1416, 1363, 1228, 1135, 994, 925, 556 cm^{-1}

Step 2



Monomer from Step 1 (1.0g) was dissolved in dry dichloromethane (3cm^3). The Irgacure 184 (10mg) was added to the solution, heated and mixed to ensure homogeneity. It was then spread evenly on an 18 x 25 cm glass plate and the solvent allowed to evaporate off to leave a thin, clear film. This was irradiated with a Philips UVA sunlamp for 30 minutes to form a hard cross-linked polymer film. This was removed (scalpel), washed in dichloromethane and dried. Yield 0.64g, 64%.

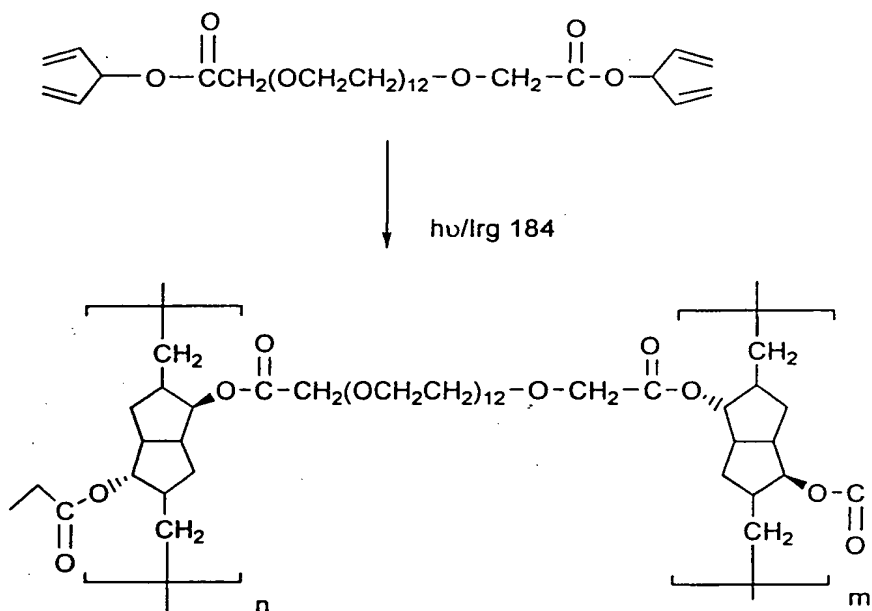
Ir v max (thin film): 3424, 2936, 2374, 2346, 1705, 1644(s), 1524, 1436(s), 1222, 1138, 992, 924, 561 cm^{-1}

Example 19Step 1

Polyethylene glycol 600 diacid (6.0g, 0.010 mol), 1,4-pentadiene-3-ol (2.0g, 0.024 mol), 1,3-dicyclohexylcarbodiimide (206.33) (4.95g, 0.024 mol) and 4-dimethylaminopyridine (300mg) were stirred together in dry dichloromethane (50ml) for 72h. The resultant 1,3-Dicyclohexyl-urea was removed by filtration and removal of solvent left a clear oil. Column chromatography using silica gel and dichloromethane - 40/60 petrol (1:1) followed by dichloromethane-methanol (1:3) gave, after removal of solvent, a colourless, clear oil. 6.73g, 85%.

$^1\text{H NMR}$ (CDCl_3) δ : 3.55-3.80 (m, 48H), 4.15 (s, 4H), 5.25-5.50 (m, 10H), 5.75-5.95 (m, 4H)

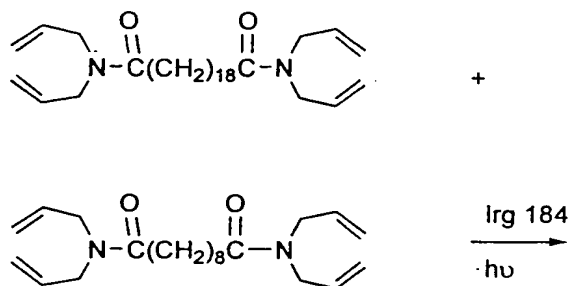
Ir v max (thin film): 2860, 1745, 1635, 1450, 1345, 1250, 1195, 1140, 1115, 990, 940, 750 cm^{-1}

Step 2

Monomer from Step 1 (1.60g, 0.0021 mol) and Irgacure 184 (21mg, 0.000105 mol) were dissolved in dry dichloromethane (3cm³) and the solution was spread over a 18 x 25cm glass plate. The solvent was allowed to evaporate to leave a thin, clear film. The film was then irradiated with a Philips UVA sunlamp (75w) to form a hard cross-linked polymer coating. The coating was removed and washed in dry dichloromethane and dried thoroughly.

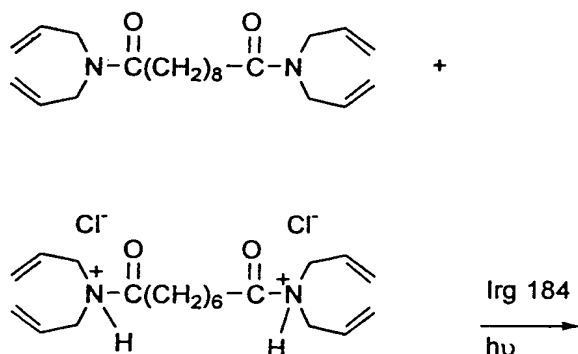
Yield 1.10 g, 67%

Ir v max (KCl disc): 2920, 2860, 1745, 1680, 1640, 1450, 1345, 1280, 1250, 1200, 1140, 1110, 950, 850 cm⁻¹.

Example 20

The Monomer of Example 12 Step 1 (0.5g) and the monomer of Example 11 Step 1, were dissolved with the Irgacure 184 (20mg) in dichloromethane (5 cm³) and the solution was spread evenly on an 18 x 25cm glass plate. The solvent was evaporated off and the residual film irradiated with the Philips UVA (75w) sunlamp for 1 hour. The resultant cross-linked copolymeric film was removed in strips (scalpel) and washed in dichloromethane, then thoroughly dried. The resultant film was soft, stretchy but of low tensile strength.

Ir v max (thin film): 3431, 2931, 2858, 1649(s), 1453, 720 cm⁻¹

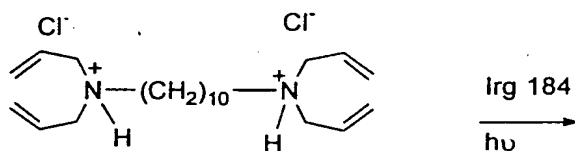
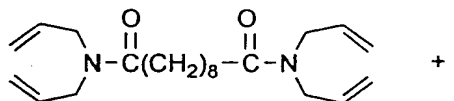
Example 21

The monomer of Example 11 Step 2 (0.5g) and monomer B above (0.5g) (prepared by analogous methods to those described above) were dissolved in dry dichloromethane (5 cm³). The Irgacure

184 (20mg) was added and the mixture warmed (water bath) until the photoinitiator had dissolved. The solution was spread evenly on an 18 x 25 cm glass plate and the solvent allowed to evaporate. The two monomers phase separated to give an even 'pimpled' effect. Attempts to mix the two monomers using dichloromethane and mechanical mixing resulted, after evaporation of solvent, in the same pimpled effect. The monomers were irradiated with the Philips UVA (75w) sunlamp for 1 hour to form a phase-separated cross-linked solid polymeric 'pimpled' film but unstable due to the discontinuity of polymerisation at each phase boundary.

Ir v max (thin film): 3421(s), 2939(s); 1642(s), 1456, 1167, 577 cm^{-1}

Example 22



Irg 184
 $\xrightarrow{h\nu}$

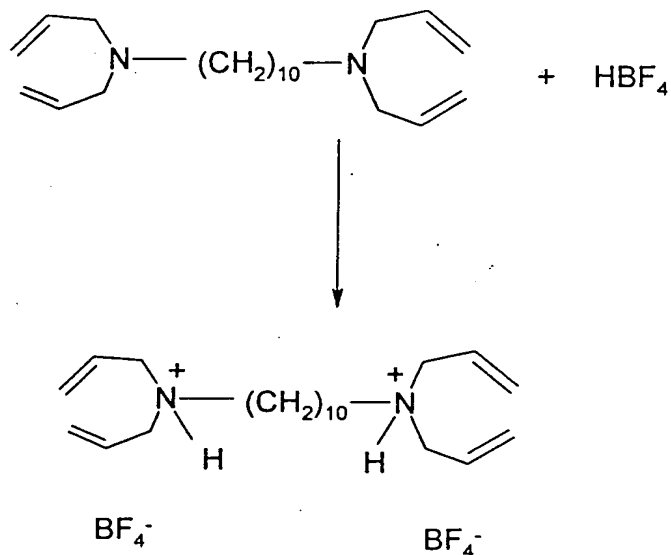
The monomer of Example 11 step 1 (0.5g) and the monomer of Example 3 Step 2 (0.5g), were dissolved with the Irgacure 184 (20mg) in dichloromethane (5 cm^3) and the solution was evenly spread on an 18 x 25 cm glass plate. The solvent was evaporated off to leave a residual clear film which was irradiated with the Philips UVA (75w) sunlamp for 1 hour. The resultant cross-linked polymer was removed in strips (scalpel) and washed in dichloromethane (50 cm^3) then thoroughly dried.

Ir v max (thin film): 3448(s), 2931, 2855, 1629(s), 1534, 1452, 1230, 731 cm^{-1} .

Example 23

Other polymerisable monomers were produced as follows:

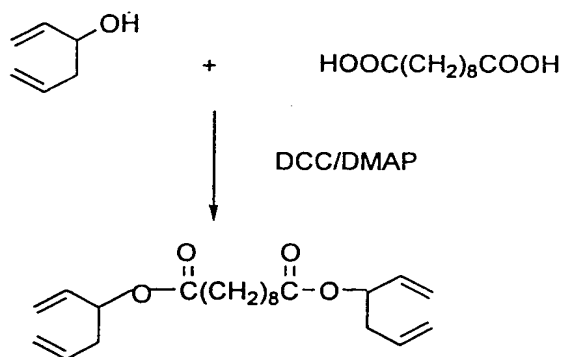
Example 23a



The monomer illustrated (5.0g) above was treated with a 50% aqueous solution of fluoroboric acid to pH 1.0 (universal indicator paper). The organic phase was extracted using dichloromethane (2 x 75 cm^3) and then dried over MgSO_4 . Removal of solvent in vacuo gave a heavy pale yellow oil. 7.40g, 97%.

$^1\text{HNMR}$ (CDCl_3) δ : 1.20(s, br, 12H), 1.65(s, br, 4H), 3.05(quin, 4H), 3.75(t, 8H), 5.55(m, 8H), 5.90(m, 4H), 7.15(s, br, 2H)

Ir v max (thin film): 3410(br), 2930, 2857, 2649, 1707, 1646, 1460, 1428, 1056.8(very strong), 952, 763 cm^{-1}

Example 23b

Using the procedure described in Example 23a, sebacic acid (10.06g, 0.050 mol), 1,5-Hexadiene-3-ol (9.80g, 0.1 mol), 1,3-dicyclohexylcarbodiimide (22.70g, 0.11 mol) and 4-dimethylaminopyridine (450 mg) were mixed together to give the desired product

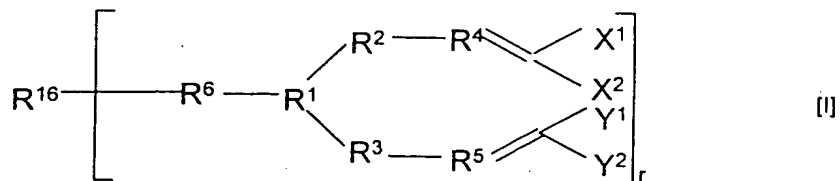
Yield: 15.6g, 87%

$^1\text{H NMR}$ (CDCl_3) δ : 1.30(s, 10H), 1.60(t, 8H), 2.35(s, 2H), 5.05-5.45(m, 10H), 5.65-5.90(m, 4H).

~~Ir v max (thin film): 2920, 2860, 1730, 1640, 1510, 1460, 1410, 1365, 1235, 1160, 1095 cm^{-1}~~

Claims

1. A compound of formula (I)



where R^1 is CH and R^6 is a bond, or R^1 and R^6 together form an electron withdrawing group;

R^2 and R^3 are independently selected from $(CR^7R^8)_n$, or a group CR^9R^{10} , $-(CR^7R^8CR^9R^{10})-$ or $-(CR^9R^{10}CR^7R^8)-$ where n is 1 or 2, R^7 and R^8 are independently selected from hydrogen or alkyl, and either one of R^9 or R^{10} is hydrogen and the other is an electron withdrawing group, or R^9 and R^{10} together form an electron withdrawing group, and

R^4 and R^5 are independently selected from CH or CR^{11} where R^{11} is an electron withdrawing group;

X^1 , X^2 , Y^1 and Y^2 are independently selected from hydrogen or fluorine;

R^{16} is a bridging group of valency r

and r is an integer of 2 or more,

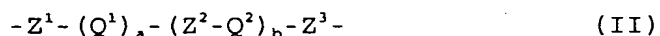
provided that at least one of (a) R^1 and R^6 or (b) R^2 and R^3 or (c) R^4 and R^5 includes an electron withdrawing group.

2. A compound according to claim 1 wherein the compound of formula (I) is curable under the influence of ultraviolet light.

3. A compound according to any one of the preceding claims wherein R^1 and R^6 form an electron withdrawing group.

4. A compound according to claim 3 wherein in the compound of formula (I), R^7 and R^8 are groups $(CR^{8'}R^8)_n$ and R^1 and R^5 are CH groups.
 5. A compound according to claim 3 or claim 4 wherein in the compound of formula (I), R^1 is a heteroatom or a substituted heteroatom which has electron withdrawing properties.
 6. A compound according to claim 6 where R^1 is a $N^+R^{12}(Z^{m-})_{1/m}$, $S(O)_pR^{13}$, B , $P(O)_qR^{14}$ or $Si(R^{15})$ where R^{12} , R^{13} , R^{14} and R^{15} are independently selected from hydrogen or hydrocarbyl, Z is a anion of valency m , p is 0, 1 or 2, and q is 0, 1, 2 or 3.
 7. A compound according to claim 7 where R^1 is a $N^+R^{12}(Z^{m-})_{1/m}$ group where R^{12} , Z and m are as defined in claim 6.
 8. A compound according to claim 6 or claim 7 where Z is halogen.
 9. A compound according to claim 7 or claim 8 where R^{12} is alkyl.
-
10. A compound according to any one of claims 1 to 5 where R^1 is a group CH and R^6 is a group $-C(O)O-$ or $-OC(O)-$.
 12. A compound according to any one of claims 1 to 4 where R^1 is a nitrogen atom and R^6 is a carbonyl group.
 13. A compound according to claim 1 or claim 2 where R^7 and R^8 are electron withdrawing groups.
 14. A compound according to claim 13 where at least one of R^2 or R^3 include suitable electron withdrawing groups R^9 and R^{10} .

15. A compound according to claim 14 wherein R⁹ and R¹⁰ together form an oxo group.
16. A compound according to any one of the preceding claims where r is an integer of from 2 to 6.
17. A compound according to claim 16 where r is an integer of from 2 to 4.
18. A compound according to any one of the preceding claims where R¹⁶ comprises a straight or branched chain alkyl groups, optionally substituted or interposed with functional groups; or siloxane groups.
19. A compound according to any one of the preceding claims where r is 2 and R¹⁶ is a group of sub-formula (II)

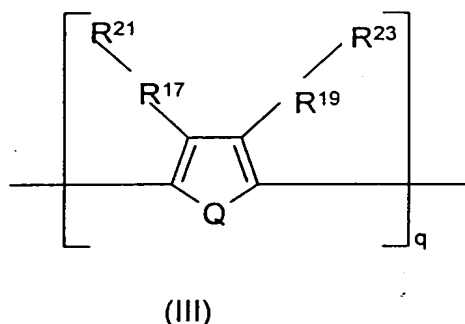


where a and b are independently selected from 0, 1 or 2, Z¹, Z² and Z³ are independently selected from a bond, an optionally substituted linear or branched alkyl or alkene chain wherein optionally one or more non-adjacent carbon atoms is replaced with a heteroatom or an amide group, Q¹ and Q² are independently selected from an optionally substituted carbocyclic or heterocyclic ring which optionally contains bridging alkyl groups; a and b are independently selected from 0, 1 or 2.

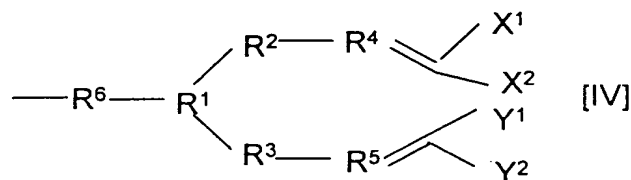
20. A compound according to any one of claims 1 to 17 wherein R¹⁶ is an electrically conducting chains.

21. A compound according to claim 20 wherein R^{16} is a tetra substituted conducting unit.

22. A compound according to claim 21 of formula (III)



where R^{21} and R^{23} are each groups of sub-formula (IV)



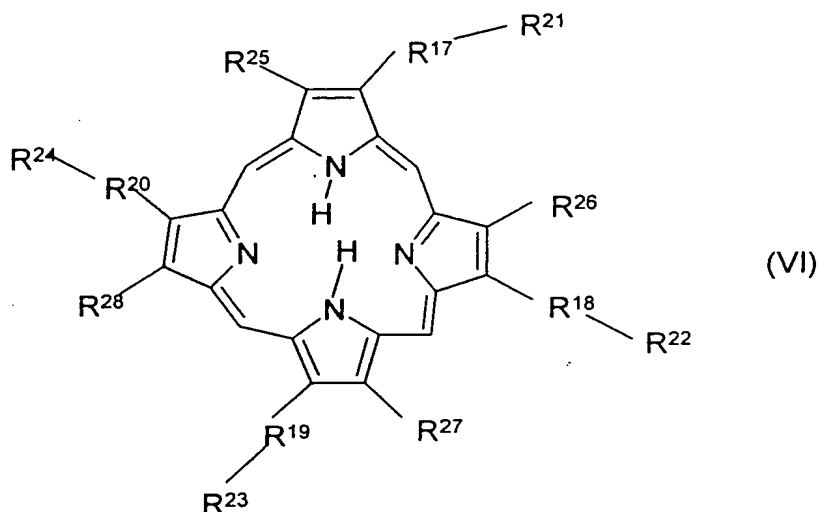
where X^1 , X^2 , Y^1 , Y^2 , R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are as defined in claim 1 and R^{17} and R^{19} are independently selected from groups of sub-formula (II) as defined in claim 19, q is an integer of 1 or more, and Q is sulphur or nitrogen.

23. A compound according to claim 22 where R^{17} , R^{18} , R^{19} and R^{20} are alkylene groups.

24. A compound according to any one of claims 1 to 17 wherein R^{16} is a tetra or octa substituted non-linear optic unit.

25. A compound according to claim 24 wherein R^{15} is an optionally substituted porphyrin or phthalocyanin wherein the optional substituents are hydrocarbyl groups.

26. A compound according to claim 25 of formula (VI)

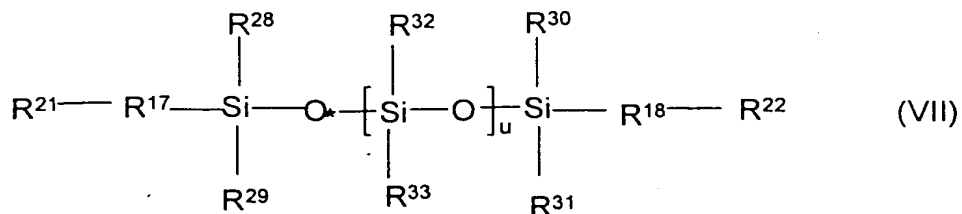


where R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , R^{23} and R^{24} are as defined in claim 22 and R^{25} , R^{26} , R^{27} and R^{28} are each independently selected from hydrogen or hydrocarbyl groups, optionally containing a metal ion within the macrocyclic heterocyclic unit.

27. A compound according to claim 26 which contains a metal ion selected from sodium or potassium.

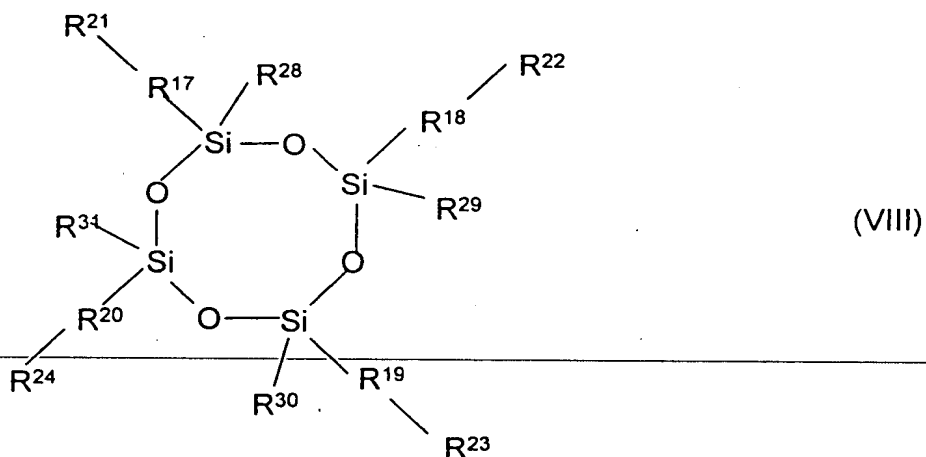
28. A compound according to any one of claims 1 to 17 wherein R^{16} is a polysiloxane network polymer where R^{16} comprises a straight or branched siloxane chain of valency r or a cyclic polysiloxane unit, or a boron equivalent thereof.

29. A compound according to claim 28 of structure (VII)



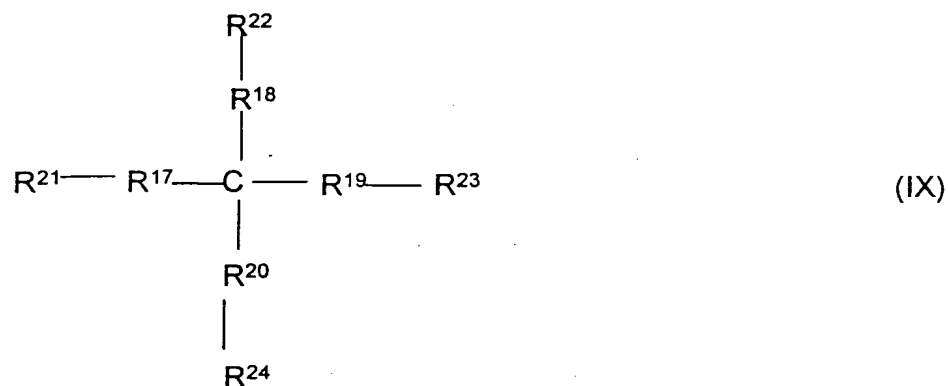
where R^{17} , R^{18} , R^{21} and R^{22} are as defined above in claim 22, R^{28} , R^{29} , R^{30} are R^{31} , are selected from hydrocarbyl and each R^{32} or R^{33} group is independently selected from hydrocarbyl or a group of formula $\text{R}^{19}-\text{R}^{23}$ where R^{19} and R^{23} are as defined above in claim 22, and u is 0 or an integer of 1 or more.

30. A compound according to claim 28 of structure (VIII)



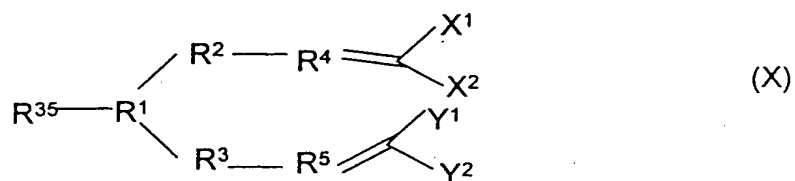
where R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , R^{23} and R^{24} are as defined in claim 22 and R^{28} , R^{29} , R^{30} and R^{31} are as defined in claim 29.

31. A compound according to any one of claims 1 to 17 of formula (IX)



where R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , R^{23} and R^{24} are as defined above in claim 22.

32. A method for preparing a compound according to any one of the preceding claims, said method comprising reacting a compound of formula (X)



where X^1 , X^2 , Y^1 , Y^2 , R^1 , R^2 , R^3 , R^4 and R^5 are as defined in claim 1, and R^{35} is hydrogen or hydroxy, with a compound of formula (XI)



where R^6 , R^{16} and r is as defined in claim 1 and Z^4 is a leaving group.

33. A method for producing a polymeric material, said method comprising causing a compound of formula (I) as defined in one of the preceding claims to polymerise.

34. A method according to claim 33 wherein the compound of formula (I) is polymerised with a different monomeric unit so as to form a copolymer.

35. A method according to claim 33 or claim 34 wherein the compound of formula (I) is a radiation curable compound and polymerisation is effected by subject the compound to the appropriate radiation.

36. A method according to claim 35 wherein the appropriate radiation is ultraviolet radiation.

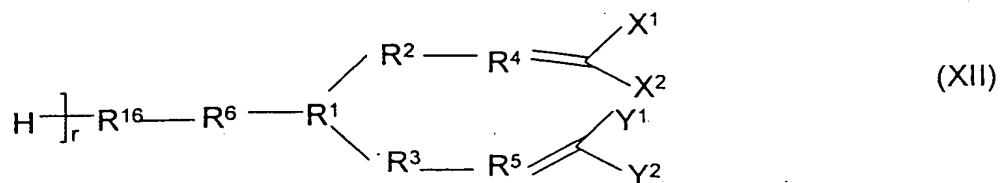
37. A method according to claim 36 which is effected in the presence of a photoinitiator.

38. A method according to claim 33 or claim 34 wherein the compound of formula (I) is a curable under the influence of an electron beam and polymerisation is effected by subjecting the compound to such a beam.

39. A method according to claim 33 or claim 34 wherein the compound of formula (I) is curable in the presence of a chemical initiator and polymerisation is effected by contacting the compound to such an initiator.

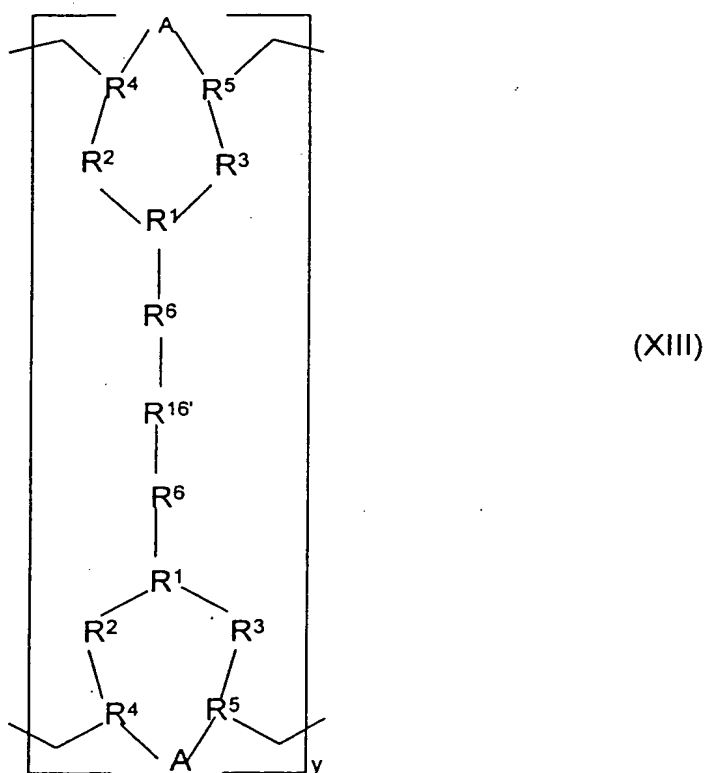
40. A method according to any one of claims 31 to 39 wherein the polymerisation is controlled by the presence of a chain terminator.

41. A method according to claim 40 where the chain terminator comprises a compound of formula (XII)

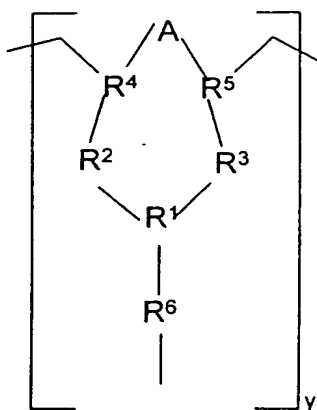


where X^1 , X^2 , Y^1 , Y^2 , R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^{16} and r are as defined in claim 1.

42. A polymeric compound of formula (XIII).



where A is a bond or or CH_2 , R^1 , R^2 , R^3 , R^4 , R^5 , R^6 are as defined in relation to formula (I), $\text{R}^{16'}$ is a group of formula R^{16} as defined in formula (I) which may be substituted by further groups of sub formula (XIV)



(XIV)

and y is an integer in excess of 1, preferably in excess of 5 and suitably from 5 to 30 and A is as defined above.

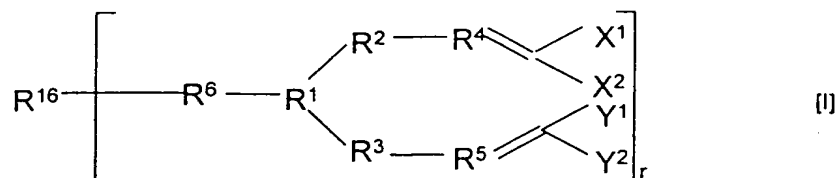
43. A polymer in accordance with claim 42 where y is an integer in excess of 5.

44. A method of forming a polymer coating on an article, which method comprises applying to the article a compound according to any one of claims 1 to 31 and allowing said compound to polymerise in situ.

45. A coated article obtainable by the process of claim 44.

Abstract

A compound of formula (I)



where R^1 is CH and R^6 is a bond, or R^1 and R^6 together form an electron withdrawing group;

R^2 and R^3 are independently selected from $(\text{CR}^7\text{R}^8)_n$, or a group CR^9R^{10} , $\text{CR}^7\text{R}^8\text{CR}^9\text{R}^{10}$ or $\text{CR}^9\text{R}^{10}\text{CR}^7\text{R}^8$ where n is 1 or 2, R^7 and R^8 are independently selected from hydrogen or alkyl, and either one of R^9 or R^{10} is hydrogen and the other is an electron withdrawing group, or R^9 and R^{10} together form an electron withdrawing group, and

R^4 and R^5 are independently selected from CH or CR^{11} where R^{11} is an electron withdrawing group;

X^1 , X^2 , Y^1 and Y^2 are independently selected from hydrogen or fluorine;

R^{16} is a bridging group of valency r

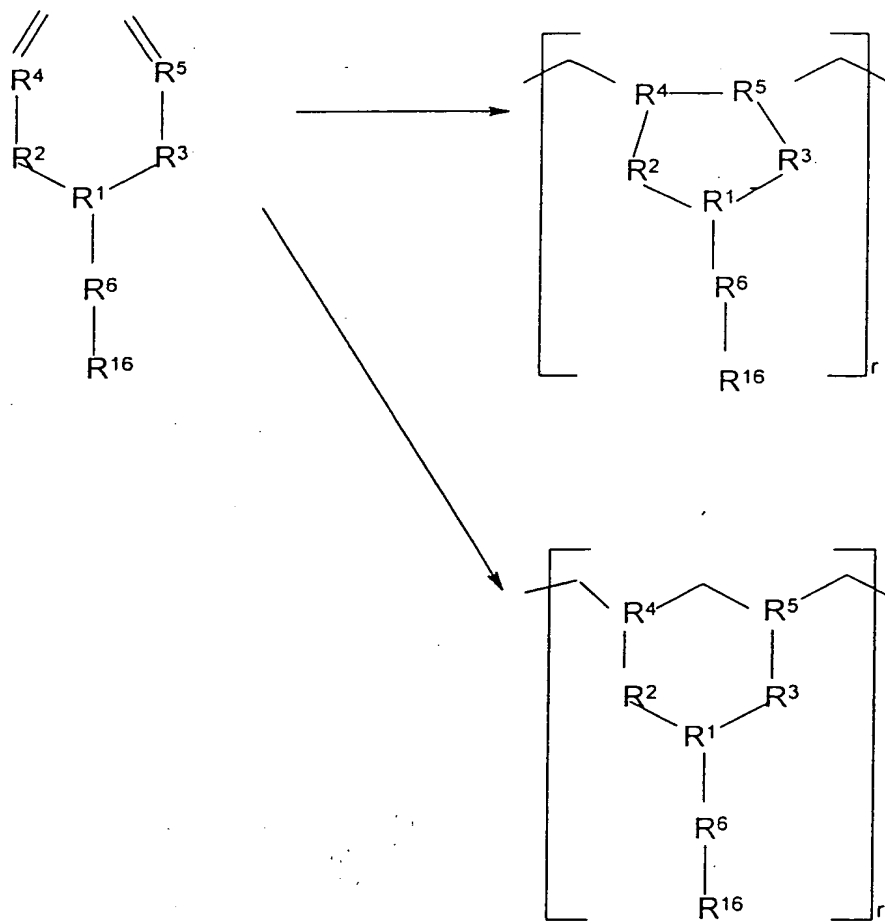
and r is an integer of 2 or more,

provided that at least one of (a) R^1 and R^6 or (b) R^2 and R^3 or (c) R^4 and R^5 includes an electron withdrawing group.

These compounds are useful in the production of network polymers, for example for coatings or binders.

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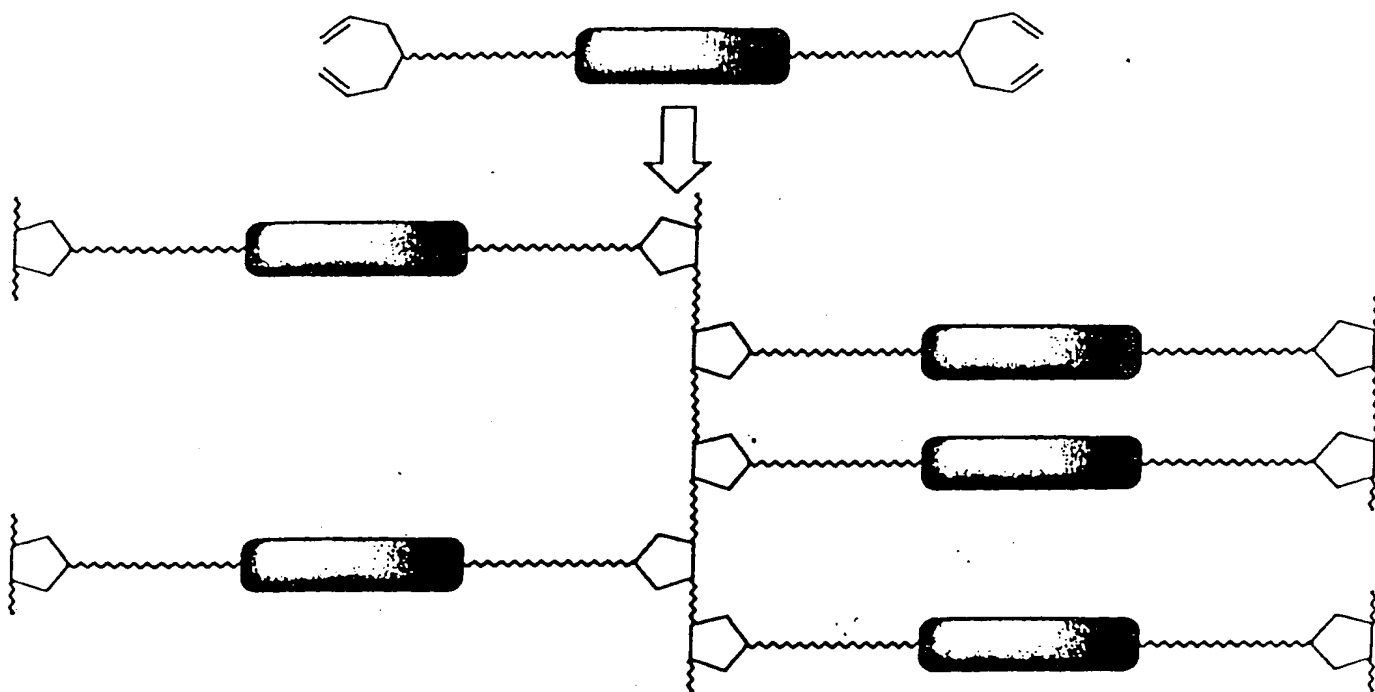
Figure 1



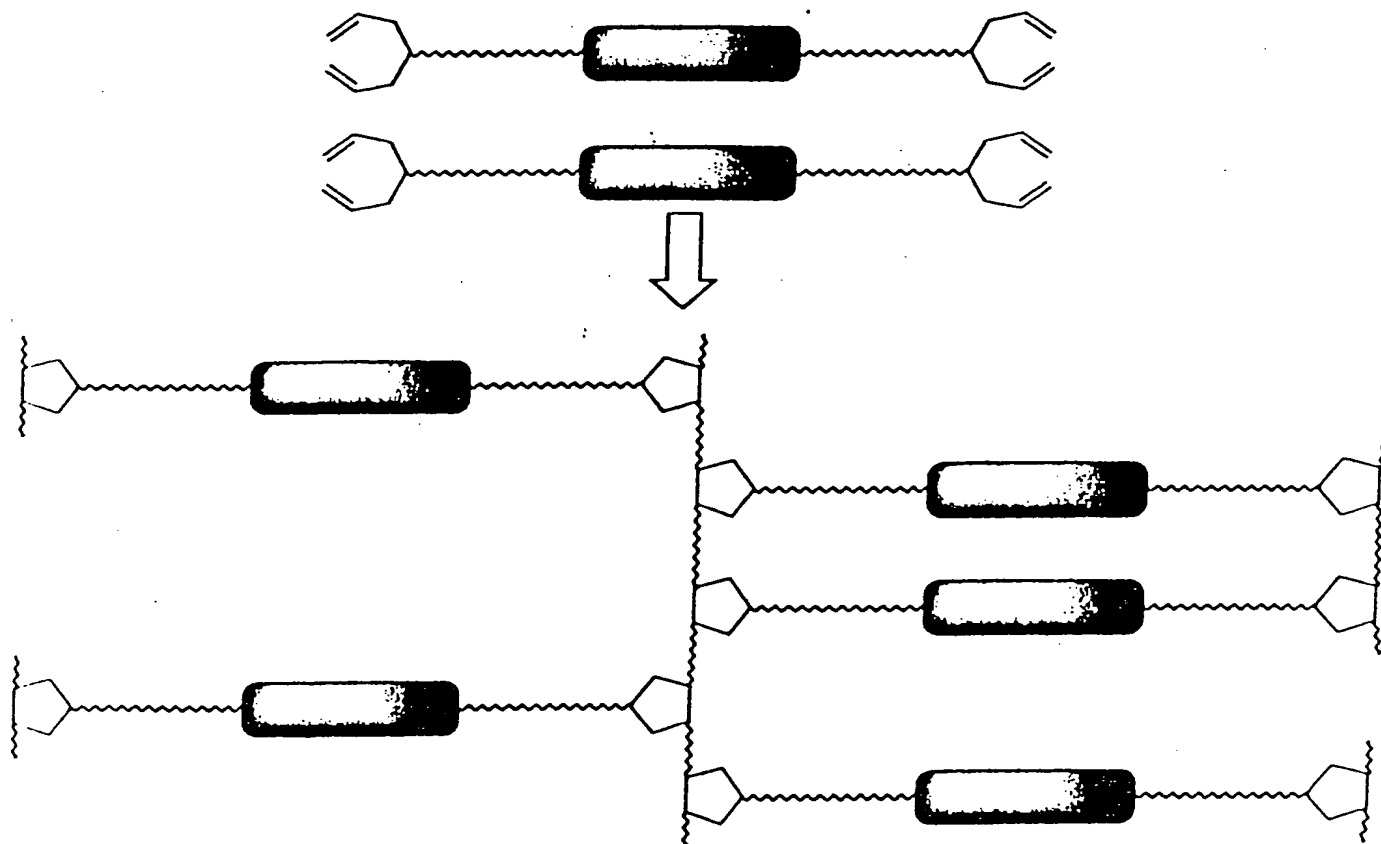
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FIGURE 2

POLYMERISATION



COPOLYMERISATION



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